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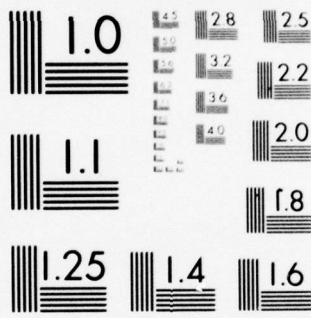
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DEVELOPMENT OF FACTS PROCEDURES FOR COMBINED CHLORINE AND OZONE IN AQUEOUS SOLUTIONS

LEVEL II

FINAL REPORT

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MARCH 1978

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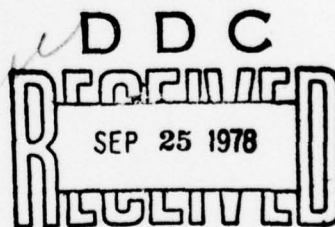[1]Department of Chemistry
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Most colorimetric procedures for chlorine analysis in treated water and wastewater suffer from the fact that they are not specific for free available chlorine. However, the FACTS (Free Available Chlorine Test with Syringaldazine) procedure is specific for free available chlorine in the presence of the common interferences found in water. This study describes the research leading to the modification of FACTS to give a procedure for total available chlorine and combined available chlorine. The modified FACTS procedure obeys Beer's Law through

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the range of 0-10 mg/l total available chlorine (as Cl_2) with a lower limit of 0.2 mg/l (as Cl_2).

Ozonation is being explored as an alternative method for disinfection. Therefore, the FACTS procedure has also been modified to determine residual ozone in aqueous solutions obeying Beer's Law through the range of 0-6 mg/l O_3 with a lower limit of 0.2 mg/l O_3.

EXECUTIVE SUMMARY

Most colorimetric procedures for chlorine analysis in treated water and wastewater suffer from the fact that they are not specific for free available chlorine. However, the FACTS (Free Available Chlorine Test with Syringaldazine) procedure is specific for free available chlorine in the presence of the common interferences found in water. This study describes the research leading to the modification of FACTS to give a procedure for total available chlorine and combined available chlorine. The modified FACTS procedure obeys Beer's Law through the range of 0-10 mg/l total available chlorine (as Cl_2) with a lower limit of 0.2 mg/l (as Cl_2).

Ozonation is being explored as an alternative method for disinfection. Therefore, the FACTS procedure has also been modified to determine residual ozone in aqueous solutions obeying Beer's Law through the range of 0-6 mg/l O_3 with a lower limit of 0.2 mg/l O_3.

ACKNOWLEDGMENTS

2

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

6

INTRODUCTION

The addition of chlorine to water and wastewater has been used as a method of disinfection in the United States continuously since the turn of the century. The predominant forms of free available chlorine that result from chlorination of water at a neutral pH are $HOCl$ and OCl^-. Ammonia in these waters will react with chlorine to produce combined available chlorine in the form of monochloramine (NH_2Cl) and dichloramine ($NHCl_2$). Trichloramine (NCl_3) may also be found in cases where a large excess of chlorine is present (e.g. superchlorination). Several laboratory procedures are available for the determination of the various forms of chlorine that occur in treated water and wastewater. Two standard procedures for determination of total available chlorine (FAC + combined available chlorine) are the iodometric method and the amperometric titration method. Both procedures rely on the production of iodine from the reaction of potassium iodide with combined chlorine. The iodometric procedure uses titration with thiosulfate to the starch-iodide end point. The amperometric procedure uses titration with phenylarsine oxide with an amperometric cell to detect the end point. There are also a number of colorimetric procedures for chlorine analysis (FAC and total available chlorine) that can more easily be adapted to field use. However, most colorimetric procedures suffer from the fact that they are not specific for free available chlorine. A newly developed method, FACTS (Free Available Chlorine Test with Syringaldazine), is specific for free available chlorine in the presence of the common interferences found in water, but has not been modified for the determination of combined or total available chlorine.

Ozone has been used as a disinfectant in Europe for many years. It has not found much use in the United States because of the difficulty in maintaining a disinfectant residual throughout the distribution system as required by law. Due to problems recently recognized with the use of chlorine, (e.g. toxicity of chlorine residuals to aquatic organisms and formation of potentially carcinogenic trihalomethanes) ozonation is being explored as an alternative method for disinfection of water in the United States. Ozone is also being considered for wastewater disinfection in treatment plants where the wastewater is intended for reuse. There is a need for a good test procedure to monitor ozone concentrations in these treated waters.

It is the intent of this research to extend the capability of the FACTS procedure to the determination of combined available chlorine, total available chlorine and ozone as they are found in water and wastewater treatment.

REVIEW OF THE LITERATURE

Chlorine

Chlorine has been used in this country on a continuing basis for water disinfection since 1908. It was originally applied in the form of the various hypochlorites; however, the use of chlorine gas predominates today.[1]

Whatever the form of chlorine used, the same chemical species will result as shown in the following equations:

Equation 1.

$$Cl_2(g) + H_2O \rightarrow HCl + HOCl$$

Equation 2.

$$NaOCl + H_2O \rightarrow Na^+ + HOCl + OH^-$$
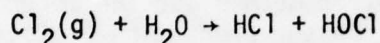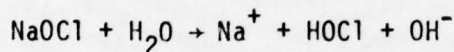
The hypochlorous acid, HOCl, formed in Equation 1 or Equation 2 is the compound desired for disinfection. Once formed, the hypochlorous acid can undergo dissociation according to the following equation:

Equation 3.

$$HOCl \rightleftharpoons H^+ + OCl^-, \qquad K_a = 2.6 \times 10^{-8} \text{ at } 20°C$$
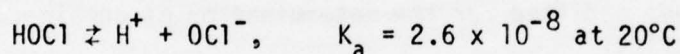
The dissociation of HOCl in H_2O at various pH levels is shown in Figure 1. It can be seen that about 80 percent of the HOCl remains undissociated at a pH of approximately 7. The sum of the HOCl, OCl^- and Cl_2 concentrations is referred to as free available chlorine (FAC). The chemical, bactericidal and virucidal properties of free available chlorine are superior to the various forms of combined available chlorine.[2] For maximum safety in the production of pathogen-free water, it is essential to chlorinate past the breakpoint, i.e. to the point of establishing a free available chlorine residual. It is the free available chlorine residual that is monitored as an indication of the safety of the water supply.

Free available chlorine is a strong oxidizing agent and will react with many organic and inorganic species in water. These reactions reduce the free available chlorine concentration and can interfere in FAC analysis. Impurities such as Fe^{+2}, H_2S, Mn^{+2} and NO_2^- are the most common inorganic interferences found in industrial wastewaters. In domestic wastewaters, the major contaminant which reacts with chlorine is ammonia. Ammonia arises from the bacterial degradation of nitrogen-containing organic compounds.

8

100
90
80
70
60
50
40
% HOCl
30
20
10

4   5   6   7   8   9   10   11

pH
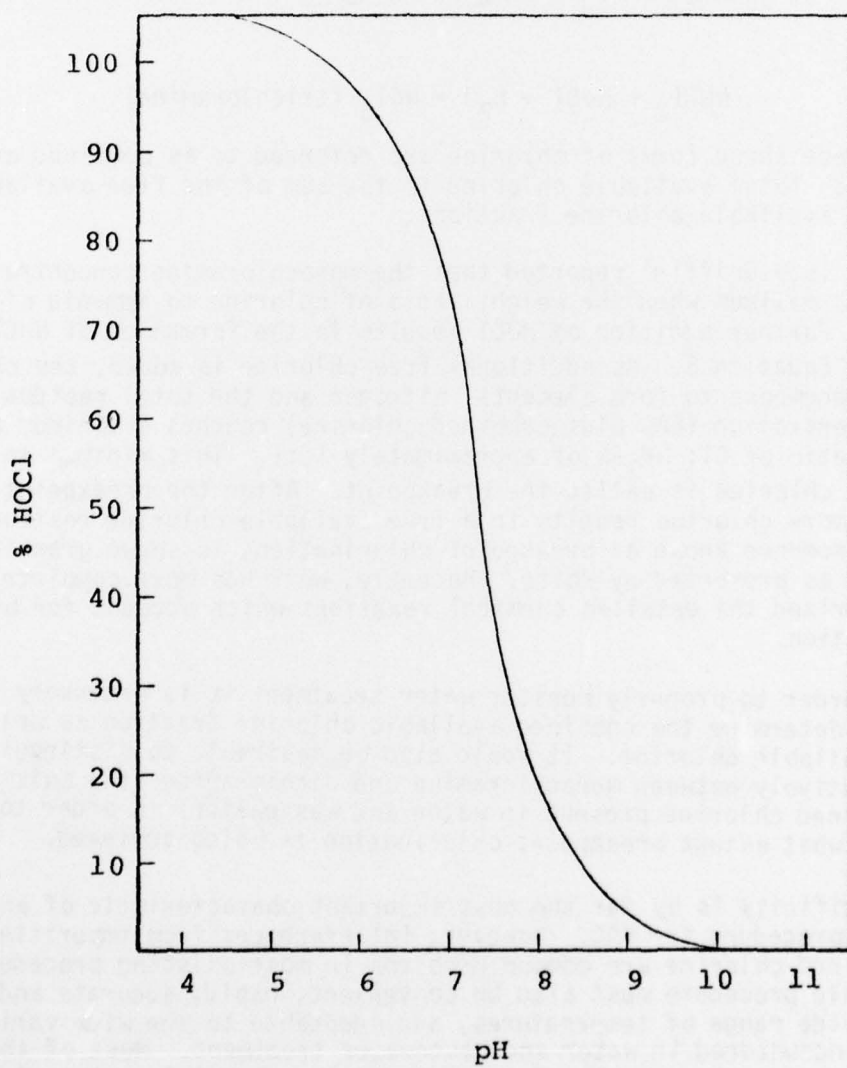
Fig. 1. Percent of HOCl undissociated
in water at 20°C with varying pH.[1]

Ammonia can react with hypochlorous acid in dilute aqueous solutions to form chloramines as shown by the following equations:

Equation 4.

$$NH_3 + HOCl \rightarrow H_2O + NH_2Cl \text{ (monochloramine)}$$

Equation 5.

$$NH_2Cl + HOCl \rightarrow H_2O + NHCl_2 \text{ (dichloramine)}$$

Equation 6.

$$NHCl_2 + HOCl \rightarrow H_2O + NCl_3 \text{ (trichloramine)}$$
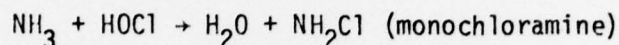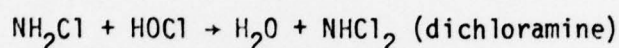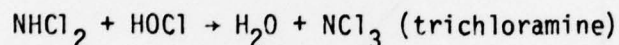
These three forms of chlorine are referred to as combined available chlorine. Total available chlorine is the sum of the free available and combined available chlorine fractions.

In 1939 Griffin[3] reported that the monochloramine concentration reaches a maximum when the weight ratio of chlorine to ammonia nitrogen is 5:1. Further addition of HOCl results in the formation of $NHCl_2$ as shown in Equation 5. As additional free chlorine is added, the chloramines decompose to form elemental nitrogen and the total residual chlorine concentration (FAC plus combined chlorine) reaches a minimum at a weight ratio of $Cl:NH_3-N$ of approximately 10:1. This minimum in total residual chlorine is called the breakpoint. After the breakpoint, addition of more chlorine results in a free available chlorine residual. This phenomenon known as breakpoint chlorination, is shown graphically in Figure 2 as presented by White.[4] Recently, Wei[5] has more completely characterized the detailed chemical reactions which account for breakpoint chlorination.

In order to properly monitor water treatment it is necessary to be able to determine the combined available chlorine fraction as well as free available chlorine. It would also be desirable to distinguish quantitatively between monochloramine and dichloramine (the chief forms of combined chlorine present in water and wastewater) in order to determine to what extent breakpoint chlorination is being achieved.

Specificity is by far the most important characteristic of any analytical procedure for FAC. However, interferences from impurities such as combined chlorine are common problems in most existing procedures.[6] An acceptable procedure must also be convenient, rapid, accurate and precise over a wide range of temperatures, and adaptable to the wide variety of waters encountered in water and wastewater treatment. Most of the existing procedures do not meet all of these criteria. A brief review of the disadvantages of some of the existing analytical procedures used in field

Fig. 2. Breakpoint Diagram after White[4]

pH 7, 10°C
2 Hr. contact time
0.5 mg/l ammonia-nitrogen

FAC
Monochloramine
Dichloramine
Trichloramine

Breakpoint

Free and combined residual

Combined chlorine
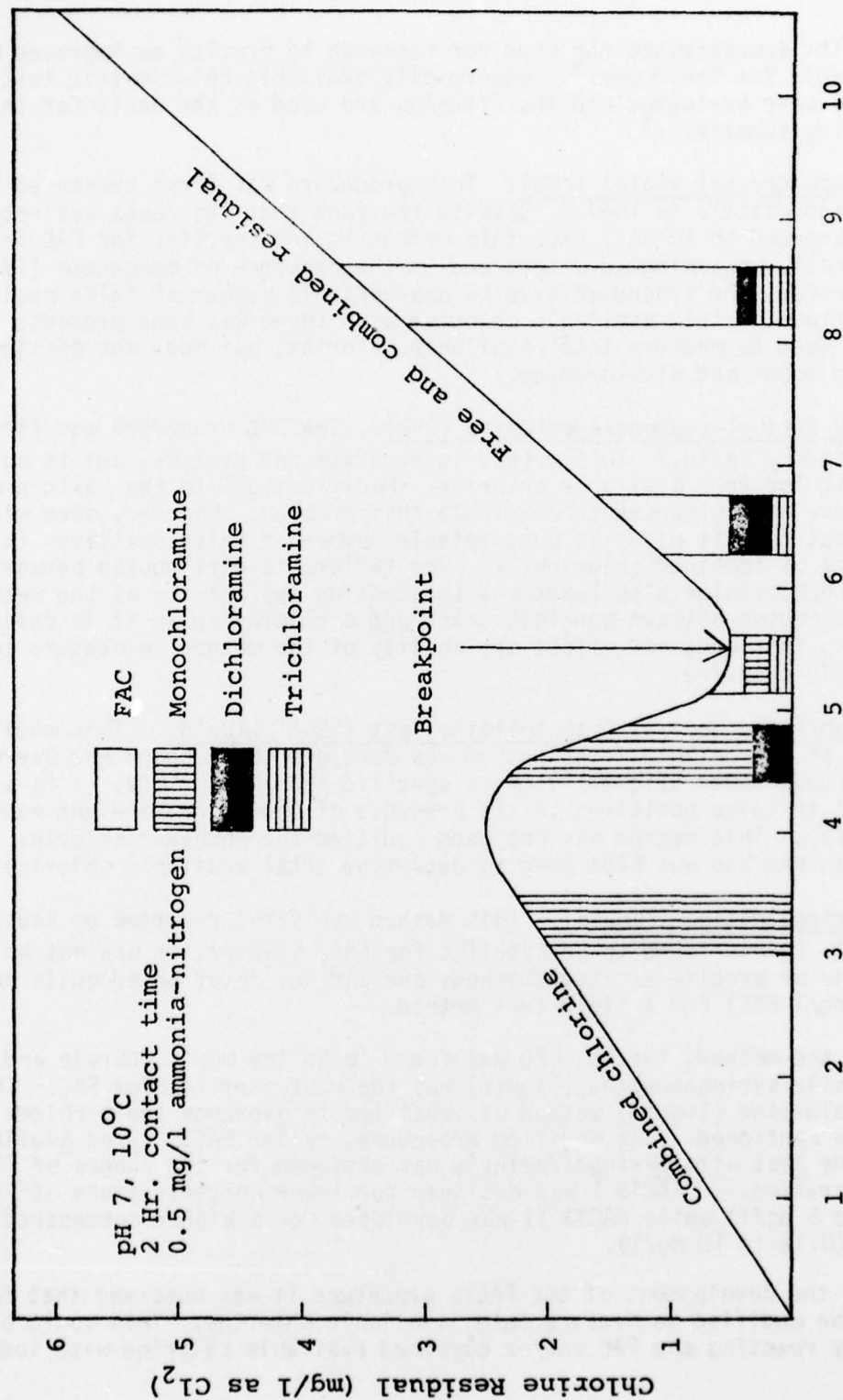
Chlorine Dosage (mg/l as Cl_2)

Chlorine Residual (mg/l as Cl_2)

test kits demonstrated the need for research to provide an improved method acceptable for field use.[7] Commercially available colorimetric test procedures were evaluated and the findings are used as the basis for the following summary.[6,7]

Leuco Crystal Violet (LCV). This procedure was first presented by Black and Whittle in 1967.[8] Despite the fact that its range has recently been extended to 10 mg/l FAC, this method is not specific for FAC in organically contaminated waters and in the presence of manganese (IV). When tested, the procedure gave an unacceptable number of false positives, indications of free available chlorine when there was none present. It can be used to measure total available chlorine, but does not distinguish between mono- and dichloramine.

N,N-Diethyl-p-phenylenediamine (DPD). The DPD procedure was first presented by Palin.[9] This method is accurate and precise, but is not specific for free available chlorine. Modifications to the basic procedure have been proposed to eliminate this problem. However, even with modifications, it gives an unacceptable number of false positives in the presence of combined chlorine.[6,7] The failure to distinguish between FAC and monochloramine also leads one to question the ability of the method to distinguish between monochloramine and dichloramine as it is designed. However, this does not effect the ability of the method to measure total available chlorine.

Stabilized Neutral Orthotolidine Test (SNORT Liquid). This modification of the orthotolidine method was developed by Johnson and Overby.[10] Even though SNORT (liquid) is more specific than DPD or LCV, it is still subject to false positives in the presence of monochloramine and manganese (IV). This method has not been modified for combined chlorine analysis and has not been used to determine total available chlorine.

Syringaldazine (liquid). This method was first reported by Bauer and Rupe.[11] It was found to be specific for FAC; however, it was not as accurate or precise as other methods and did not cover an adequate range (0-10 mg/l FAC) for a field test method.

Of the methods tested, DPD was found to be the most accurate and precise while syringaldazine (liquid) was the most specific for FAC. The syringaldazine (liquid) method was modified to overcome the problems previously mentioned. The modified procedure, called FACTS (Free Available Chlorine Test with Syringaldazine), was designed for two ranges of FAC concentration.[12] FACTS I was designed for lower concentrations of FAC (0.1 to 5 mg/l) while FACTS II was developed for a higher concentration range (0.15 to 10 mg/l).

In the development of the FACTS procedure it was observed that FACTS might be modified to measure total available chlorine. This could be done by reacting the FAC and/or combined available chlorine with iodide

to give iodine which could be analyzed with the FACTS procedure. The reaction of iodide with HOCl and NH_2Cl is shown in the following equations:

Equation 7.

$$I^- + HOCl \rightarrow HOI + Cl^-$$

Equation 8.

$$I^- + NH_2Cl + H_2O \rightarrow HOI + Cl^- + NH_3$$
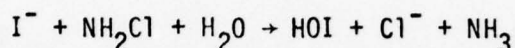
The HOI oxidizes syringaldazine to produce a product with the same absorption maximum as that produced in the reaction of syringaldazine with chlorine.

Ozone

Studies show that trihalomethanes, most notably chloroform, occur in chlorinated drinking waters and wastewater.[13-15] Chlorine residuals in relatively small concentrations (less than 0.1 mg/l) in wastewaters have been shown to be toxic to various forms of aquatic life.[16,17] As a result, alternative methods of disinfection are being explored. One alternative method is application of ozone by passing a mixture of air and ozone, or oxygen and ozone through the water to be treated. In aqueous solution ozone has been found to be an excellent bactericide and virucide.[18] The standard reduction potential of ozone in water, as presented in Table I, is greater than other disinfectants. Because of the reactivity of ozone in aqueous solutions it is not surprising to find that it is an effective disinfectant.

Besides being a very powerful oxidizing agent, ozone has other advantages. For example, the use of ozone avoids many taste and odor problems often encountered with chlorination procedures.[19] The oxygen released when ozone is reduced can act to increase the oxygen level of the water, improve sewage treatment and promote aquatic life in the receiving stream.

Although ozone is widely used for treatment in Europe, this is not the case in the United States.[19] Several factors have prevented its use. These include the high cost of ozone generation and the fact that ozone leaves no residual in the treated water. Also of importance for any disinfectant is the need for an analytical procedure to measure low concentrations of the disinfectant in water. The analytical procedures for ozone are hampered by several factors. For example, any method of analysis requiring too much time from sample collection to analysis will result in erroneously low ozone measurements[20] because of the relatively rapid decomposition of ozone in water.

Table I Standard Oxidation-Reduction Potentials
of Ozone and Titratable Species of Halogens[5]

Reaction	Value of E_o in Volts
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$HOBr + H^+ + 2e^- \rightarrow Br^- + H_2O$	1.33
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	1.24
$ClO_2 + e^- \rightarrow ClO_2^-$	1.15
$Br_2 + 2e^- \rightarrow 2 Br^-$	1.07
$HOI + H^+ + 2e^- \rightarrow I^- + H_2O$	0.99
$ClO_2 + e^- \rightarrow ClO_2^-$	0.95
$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.90
$OBr^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	0.70
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$I_3^- + 2e^- \rightarrow 3I^-$	0.53
$OI^- + H_2O + 2e^- \rightarrow I^- + 2OH^-$	0.49

14

The current standard method for aqueous ozone analysis involves the oxidation of iodide to iodine in the presence of excess iodide.[21] This reaction is shown by the following equation:

Equation 9.

$$O_3 + 2I^- + H_2O \rightleftharpoons I_2 + O_2 + 2OH^-$$
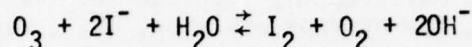
The iodine liberated is titrated with standard thiosulfate solution to the starch-iodide end point. It allows little time for loss of ozone to the atmosphere since the sample can be immediately fixed with potassium iodide. The large volumes of sample required for low ozone concentrations (less than 0.1 ppm) are inconvenient. They are troublesome, but can be tolerated if a method gives reliable and reproducible results.

Equation 9 indicates a stoichiometric ratio of one molecule of iodine liberated per molecule of ozone absorbed in the KI solution. Several workers have recently reported data that verifies this ratio.[22-24] Others have reported data indicating that this volumetric method results in a ratio exceeding 1:1 at extreme pH.[25-27]

Aqueous ozone solutions have been analyzed by the standard volumetric procedure and by a spectrophotometric method.[25] In every case the standard volumetric method gave higher results. The higher ozone measurements have been attributed to the liberation of additional iodine upon acidification of the sample prior to titration. At this lower pH, it is possible that the oxygen produced as shown in Equation 9 reacts to produce additional I_3^- according to the following equation:

Equation 10.

$$6I^- + O_2 + 4H^+ \rightleftharpoons 2I_3^- + 2H_2O$$
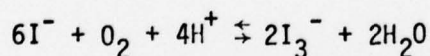
A ratio greater than 1:1 has also been attributed to the presence of the ozonide ion O_3^-, an intermediate formed by the decomposition of ozone.[26] As the pH is lowered an increasing amount of the ozonide ion will be protonated to form HO_3. The HO_3 may then react to produce additional iodine according to the following equation:

Equation 11.

$$HO_3 + I^- \rightleftharpoons HO_3^- + 1/2 I_2$$
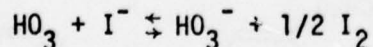
The HO_3^- produced in Equation 11 can then react to liberate additional iodine according to Equation 12.

15

Equation 12.

$$HO_3^- + I^- + 2H^+ \rightarrow HO_2 + H_2O + 1/2\ I_2$$
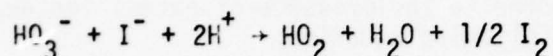
Similar conclusions were reached when UV absorption spectra of ozone solutions were seen to decrease more rapidly than the solutions' ability to liberate iodine.[28] However, the hydroperoxyl ion, HO_2^-, was suspected to be the decomposition product resulting in the liberation of additional ozone.

Studies have shown that a stoichiometric ratio of one iodine molecule to one ozone molecule is obtained if the iodine is liberated in a solution buffered at pH 7.[23,24,29] An analytical method for ozone has been developed in which the iodine liberated by ozone in a buffered (pH 7) KI solution[25] is determined spectrophotometrically as the triiodide ion, I_3^-. In excess potassium iodide, the iodine forms triiodide ion, I_3^-, which absorbs light at 352 nm. Ozone concentrations are obtained from standard curves of absorbance versus ozone concentration and/or triiodide concentration. Ozone concentrations in the range of 0 to 2.5 mg/l have been measured with this method.

RESULTS AND DISCUSSION

Chlorine

At pH 7 syringaldazine reacts with FAC to produce a stable colored product according to the following equation:

Equation 13.
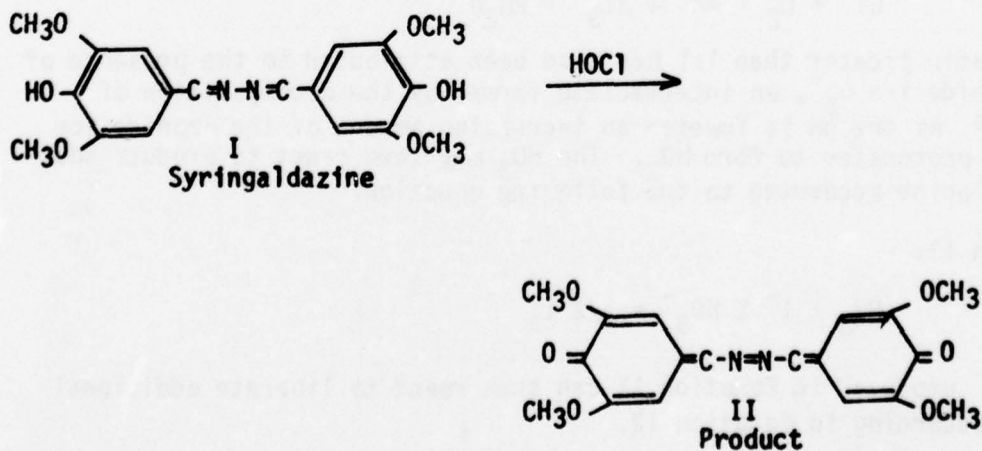
The absorption maximum for the product is 530 nm. Syringaldazine also reacts quantitatively with iodine at pH 7 to produce a product with the same absorption maximum; however, no effort has been made to verify that the same reaction product is produced. The color reactions with iodine and FAC both obey Beer's Law at low concentrations.

As shown by Equations 7 and 8, FAC and combined available chlorine react with iodide to produce iodine. The reaction of both FAC and monochloramine with iodide is quantitative over a wide range of pH. However, dichloramine reacts quantitatively only at a pH of 4 or less. Therefore, if iodine is liberated at pH 4 and subsequently reacted with syringaldazine at pH 7, total available chlorine can be determined.

Potassium Iodide Addition. To determine the amount of potassium iodide needed to react quantitatively with combined available chlorine, solutions of varying monochloramine concentration were reacted with varying amounts of potassium iodide. The FACTS procedure was used to determine the concentration of iodine liberated. The iodine concentration is proportional to the monochloramine concentration. The experimental procedure involved the following steps:

1. Five ml samples of a known monochloramine solution were pipeted into chlorine demand-free test tubes.

2. Potassium iodide solutions varying in concentration from 0.01234 g/l to 12.34 g/l were then added. Demand-free water was added to keep the final volume in the test tube constant. The total volume of the potassium iodide solution and demand-free water was always 0.5 ml. After addition, the tube was capped and inverted to mix.

3. Two tenths ml of pH 6.6 buffer (0.5 M phosphate) was then added and the tube capped and inverted to mix.

4. Two ml of syringaldazine indicator solution was added and the tube was capped and inverted twice to mix.

5. One minute after addition of the syringaldazine the absorbance of the solution at 530 nm was then read on a spectrophotometer. Color development and fading were monitored as a function of time.

The results of these "spectrophotometric" titrations of monochloramine with iodide are graphed in Figures 3 through 6. The stoichiometry of the reaction is illustrated by the mole ratio of potassium iodide to monochloramine required for maximum color development. These values were calculated from the ratios observed at the intercepts of the two straight lines shown in each curve. These results are shown in Table II.

17
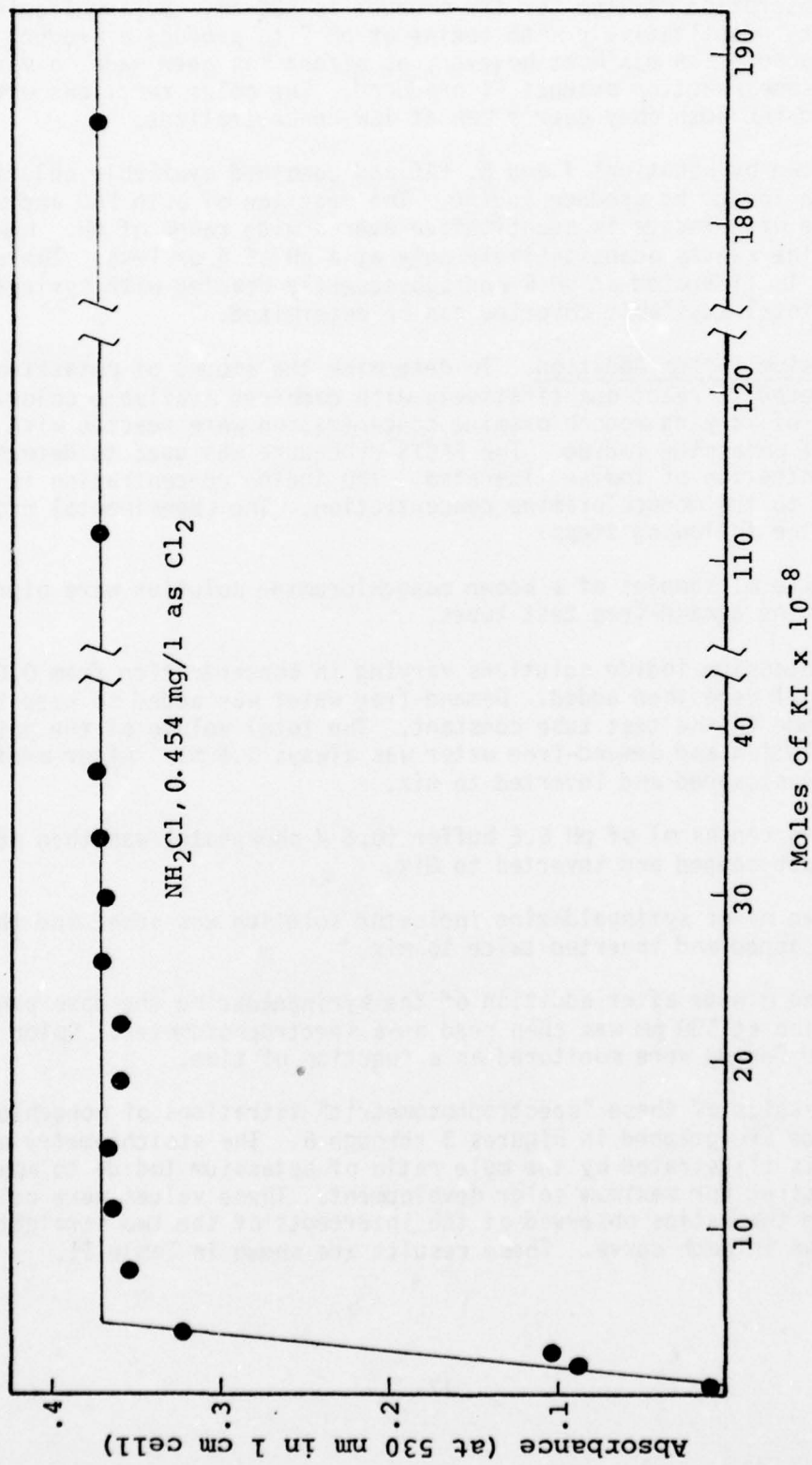
Fig. 3. Response of monochloramine to the modified FACTS procedure with
varying amounts of KI.
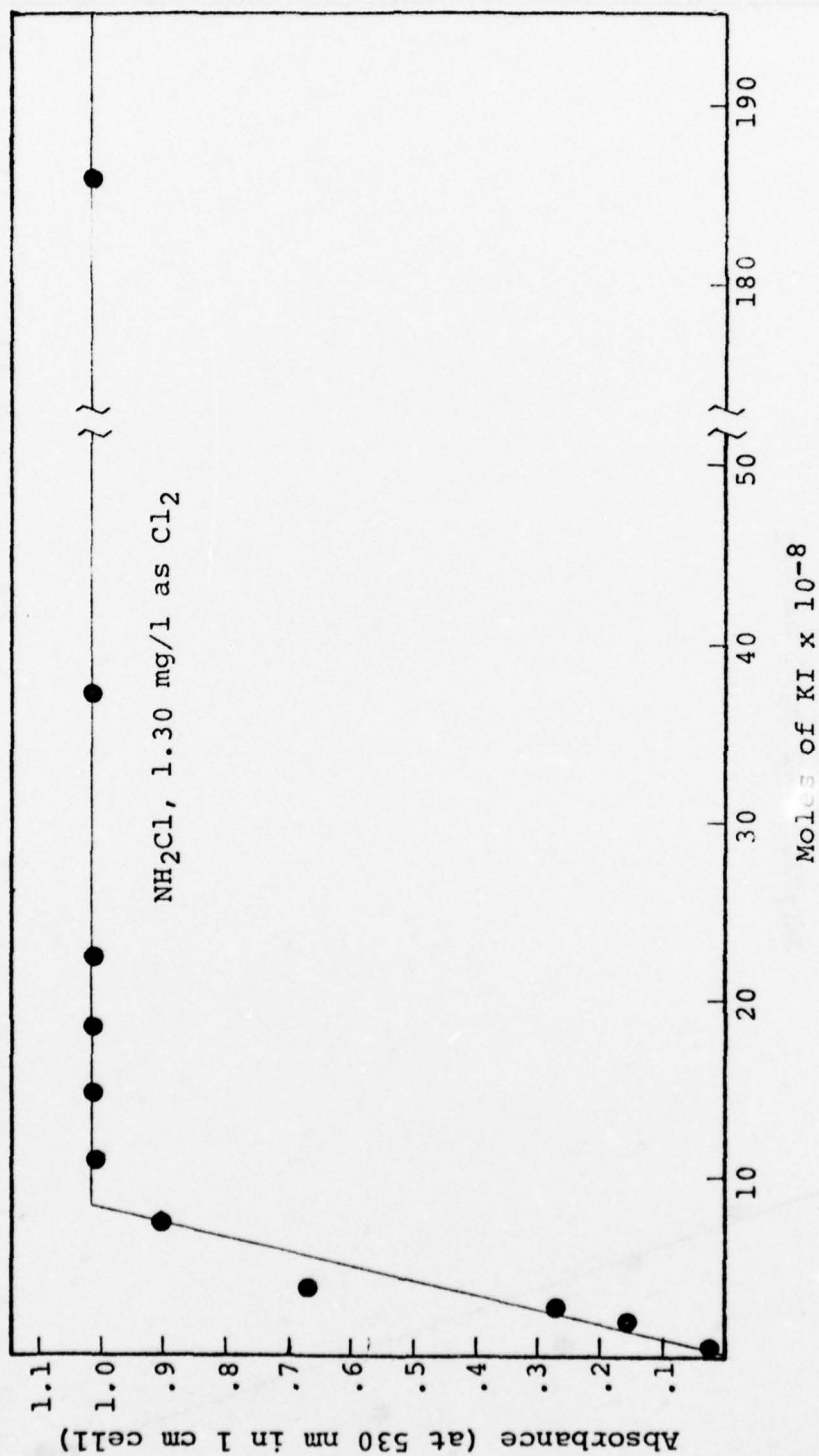
Fig. 4. Response of monochloramine to the modified FACTS procedure with varying amounts of KI.
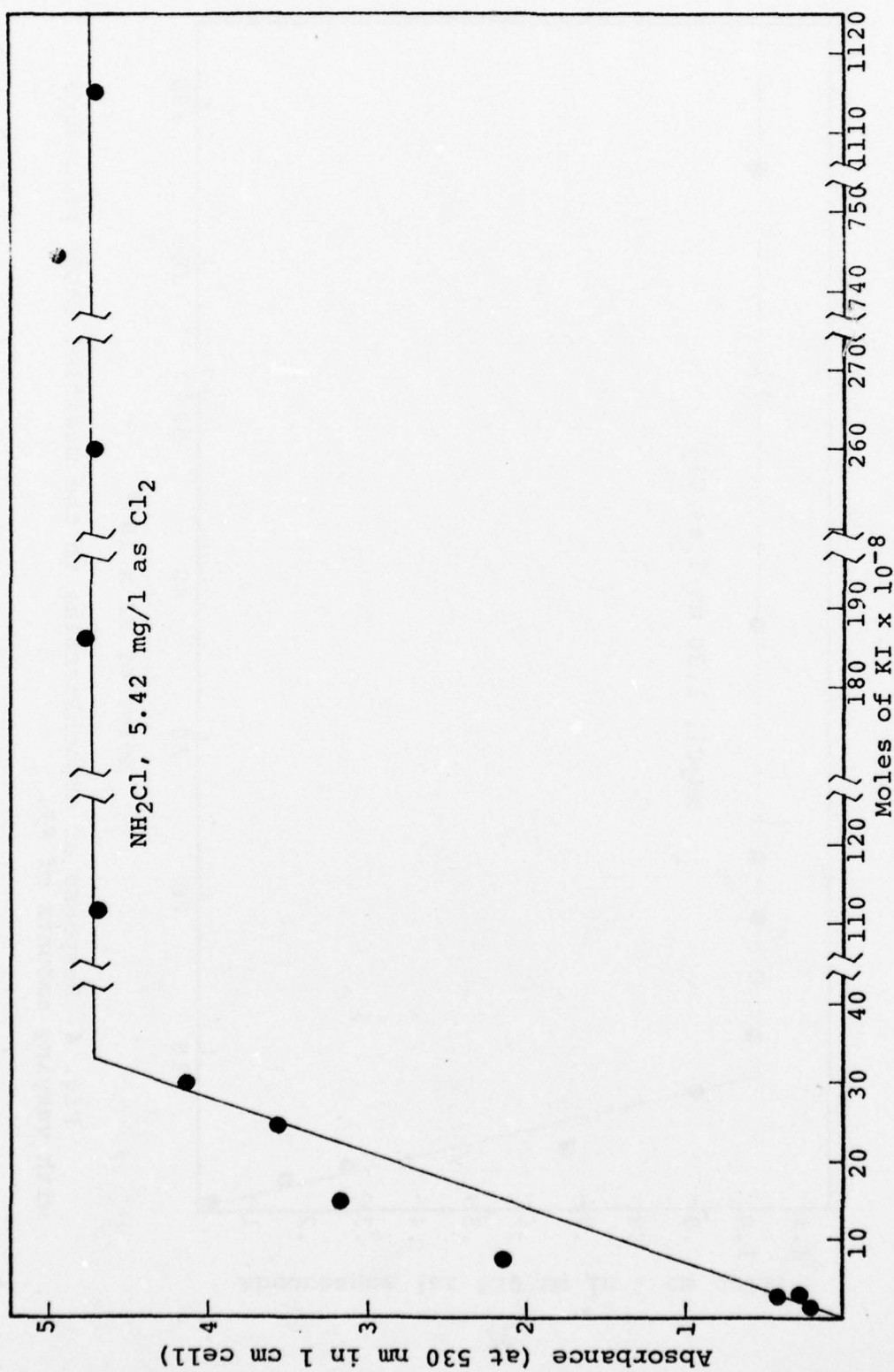
Fig. 5. Response of monochloramine to the modified FACTS procedure with varying amounts of KI.
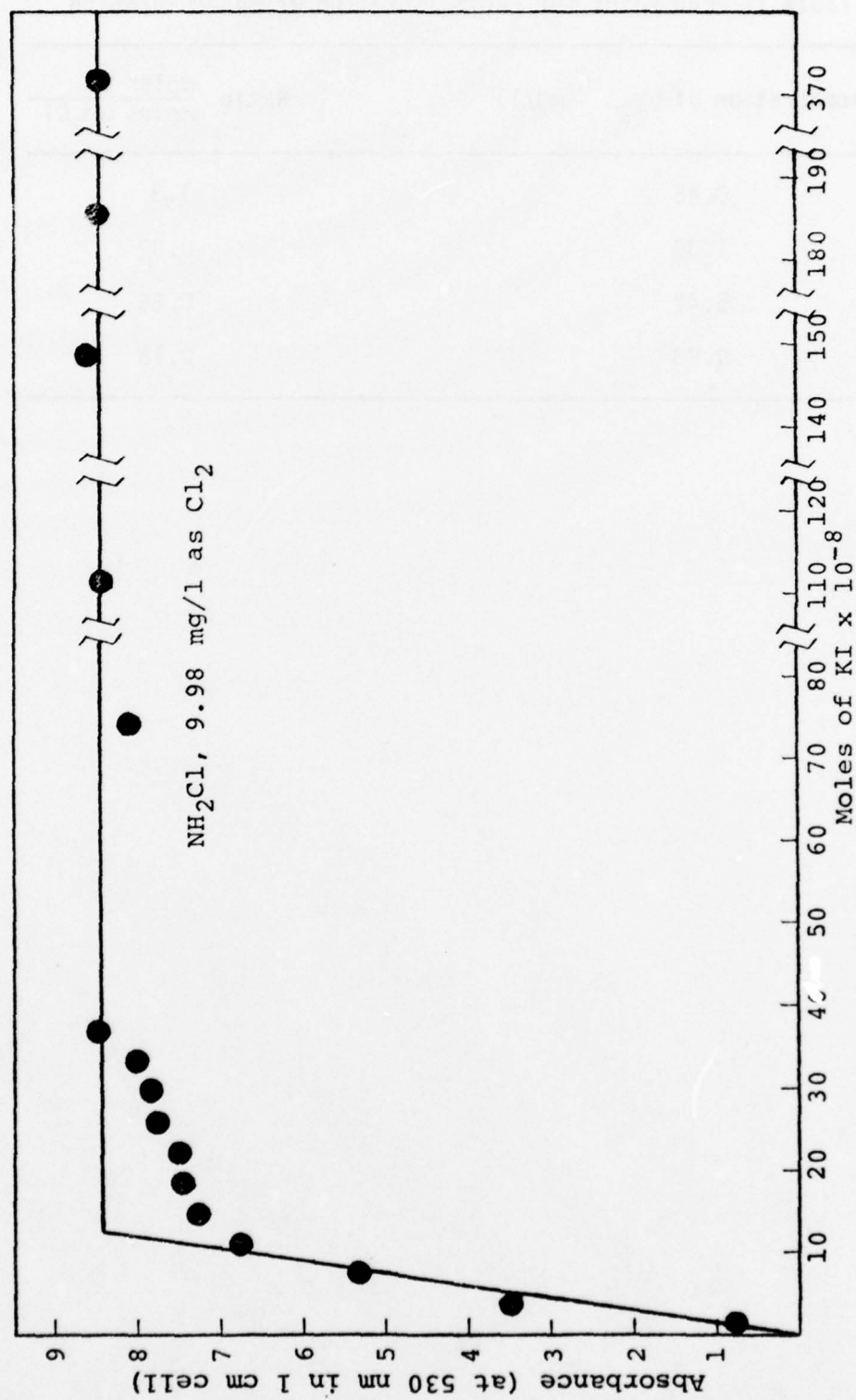
Fig. 6. Response of monochloramine to the modified FACTS procedure with varying amounts of KI.

Table II End Point for FACTS Titration of Monochloramine

Concentration of NH_2Cl (mg/l)	Ratio $\dfrac{\text{moles KI}}{\text{moles } NH_2Cl}$
0.45	1.3
1.30	0.92
5.42	0.85
9.98	0.18

Sample Calculation

$$NH_2Cl \text{ (moles)} = C \frac{V_1 N_1}{V_2} V_T$$

where

V_1 = ml of phenylarsine oxide added in amperometric titration.

N_1 = normality of phenylarsine oxide supplied with the Fischer & Porter amperometric titrator.

V_2 = ml of monochloramine solution amperometrically titrated.

V_T = l of monochloramine solution in test procedure.

C = conversion factor for changing from normality to molarity.

For Figure 3 -

$$\text{Moles } NH_2Cl = \frac{(.45)(.00564)}{200} \times .005 \times .5 = 3.2 \times 10^{-8} \text{ moles}$$

$$\text{ratio:} \quad \frac{\text{moles KI}}{\text{moles } NH_2Cl} = \frac{4.3 \times 10^{-8}}{3.2 \times 10^{-8}} = \frac{1.3}{1}$$

The data in Table II demonstrate that at low concentrations of monochloramine the molar ratio of KI to NH_2Cl was approximately 1. However, the ratio decreased with increasing monochloramine concentration indicating that the iodide ion may become catalytic at the higher monochloramine concentrations. A possible mechanism that would explain this catalytic effect of the iodide ion is as follows:

Step (1): $NH_2Cl + I^- + H_2O \rightarrow NH_3 + HOI + Cl^-$

Step (2): $HOI + SYR \text{ (reduced)} \rightarrow SYR \text{ (oxidized)} + I^-$
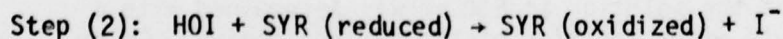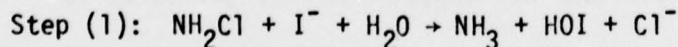
The slope in the Beer's Law region of Figures 3-6 changes considerably with increasing monochloramine concentration. At higher monochloramine concentrations (see Fig. 6) the form of this curve also changes to yield an s-shaped segment near the end point. This can effect the end point determination since two different intercepts can be selected depending upon which data points in the s-shaped segment are selected for drawing the "Beer's Law" portion of the curve. The gradual change in curve

23

shape with increasing monochloramine concentration could be indicative of a change in mechanism of the reaction. What may be happening is that as the ratio of KI to NH_2Cl increases the reaction mechanism changes from a catalytic to a stoichiometric process. No systematic study was undertaken to explain this phenomenon.

Spectrophotometric titrations of various concentrations of dichloramine with iodide ion were not carried out. At the pH necessary for quantitative reaction of dichloramine with iodide (pH $\approx$ 4) the rate of the reaction was observed to be considerably slower than that of monochloramine with iodide. For this reason an excess of potassium iodide must be added to obtain the maximum color rapidly. An excess of potassium iodide also produced an immediate quantitative response for solutions of monochloramine.

Optimum pH. Solutions of monochloramine and dichloramine of approximately equal concentrations were reacted with a constant amount of potassium iodide at varying values of pH. The liberated iodine was then reacted with syringaldazine and the color produced was followed spectrophotometrically. The experimental procedure involved the following sequence of steps:

1. A 5 ml sample of monochloramine was pipeted into a 10 cm test tube.

2. Two tenths ml of appropriate buffer solution (pH ranged from 2 to 7) was added and the tube was capped and inverted to mix. The pH of this mixture was measured with a pH meter.

3. Four tenths ml of potassium iodide solution (12.34 g/l KI) was added and the tube was capped and inverted to mix.

4. Two tenths ml of pH 6.6 buffer (0.5 M phosphate) was added and the tube was capped and inverted to mix. The pH of this mixture was measured with a pH meter.

5. Two ml of syringaldazine indicator solution (118 mg/l in 2-propanol) was then added and the tube was capped and inverted twice to mix.

6. The absorbance of the solution at 530 nm was determined with a spectrophotometer 1 minute after addition of the syringaldazine. Color development and fading were also monitored as a function of time.

The results are shown graphically in Figure 7. As expected, monochloramine reacted quantitatively with iodide over the entire range of pH examined. However, the dichloramine did not react quantitatively with

24
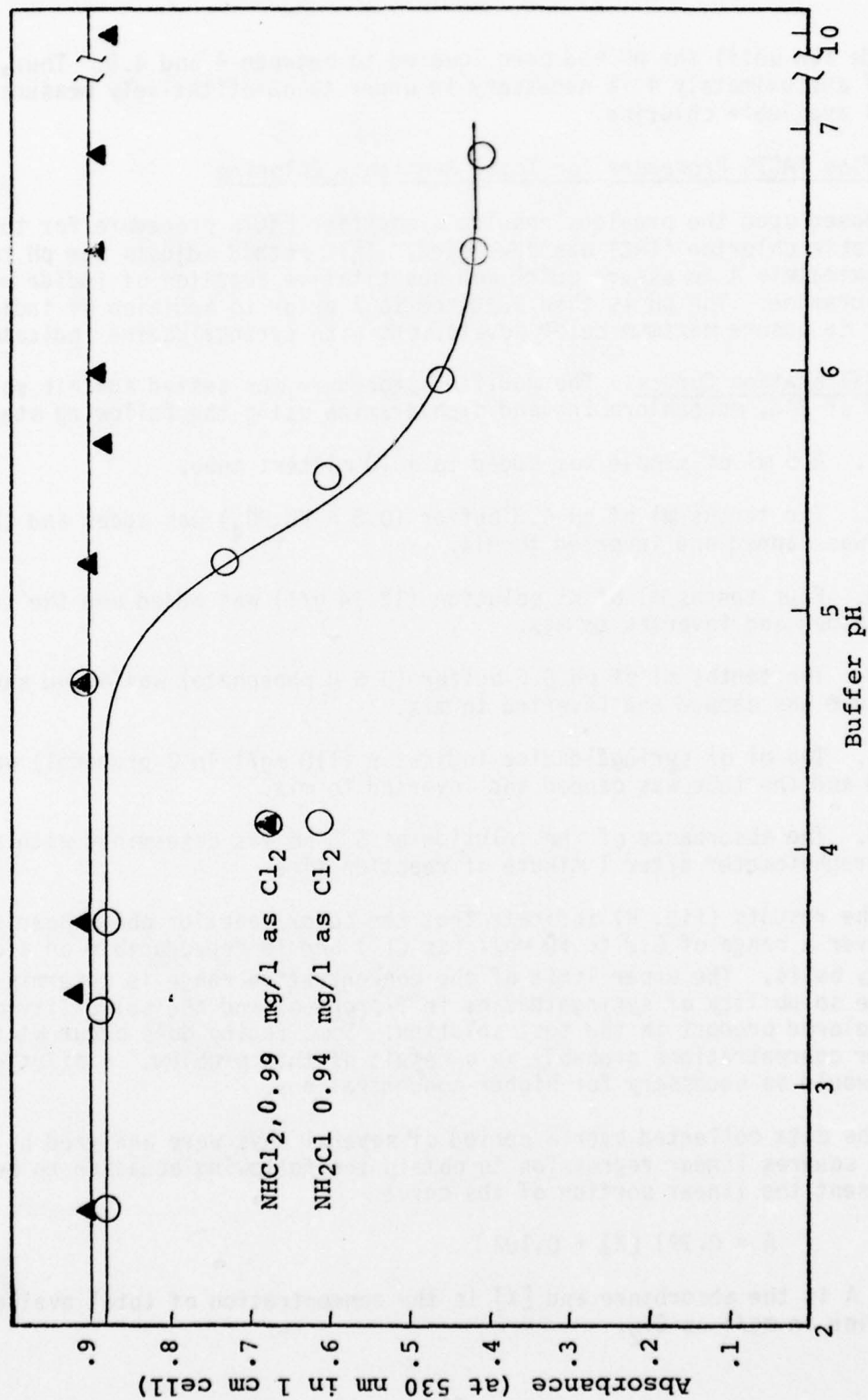
Fig. 7. Response of monochloramine and dichloramine to the modified FACTS procedure with varying pH.

NHCl2, 0.99 mg/l as Cl2 ●

NH2Cl 0.94 mg/l as Cl2 ○

Buffer pH

Absorbance (at 530 nm in 1 cm cell)

iodide ion until the pH had been lowered to between 4 and 4.5. Thus, a pH of approximately 4 is necessary in order to quantitatively measure total available chlorine.

Modified FACTS Procedure for Total Available Chlorine

Based upon the previous results a modified FACTS procedure for total available chlorine (TAC) was developed. This method adjusts the pH to approximately 4 to assure quick and quantitative reaction of iodide with dichloramine. The pH is then adjusted to 7 prior to addition of indicator to assure maximum color development with syringaldazine indicator.

Calibration Curves. The modified procedure was tested against solutions of FAC, monochloramine and dichloramine using the following steps:

1. A 5 ml of sample was added to a 10 ml test tube.

2. Two tenths ml of pH 4.3 buffer (0.5 M KH_2PO_4) was added and the tube was capped and inverted to mix.

3. Four tenths ml of KI solution (12.34 g/l) was added and the tube was capped and inverted to mix.

4. Two tenths ml of pH 6.6 buffer (0.5 M phosphate) was added and the tube was capped and inverted to mix.

5. Two ml of syringaldazine indicator (118 mg/l in 2-propanol) was added and the tube was capped and inverted to mix.

6. The absorbance of the solution at 530 nm was determined with a spectrophotometer after 1 minute of reaction time.

The results (Fig. 8) indicate that the color reaction obeys Beer's Law over a range of 0.2 to 10 mg/l (as Cl_2) and is reproducible on a day to day basis. The upper limit of the concentration range is determined by the solubility of syringaldazine in 2-propanol and the solubility of the colored product in the test solution. Some fading does occur at the higher concentrations probably as a result of this problem. A dilution step would be necessary for higher concentrations.

The data collected over a period of several days were analyzed by least squares linear regression to obtain the following equation to best represent the linear portion of the curve:

$$A = 0.791 [X] + 0.102$$

where A is the absorbance and [X] is the concentration of total available chlorine in mg/l as Cl_2.

26
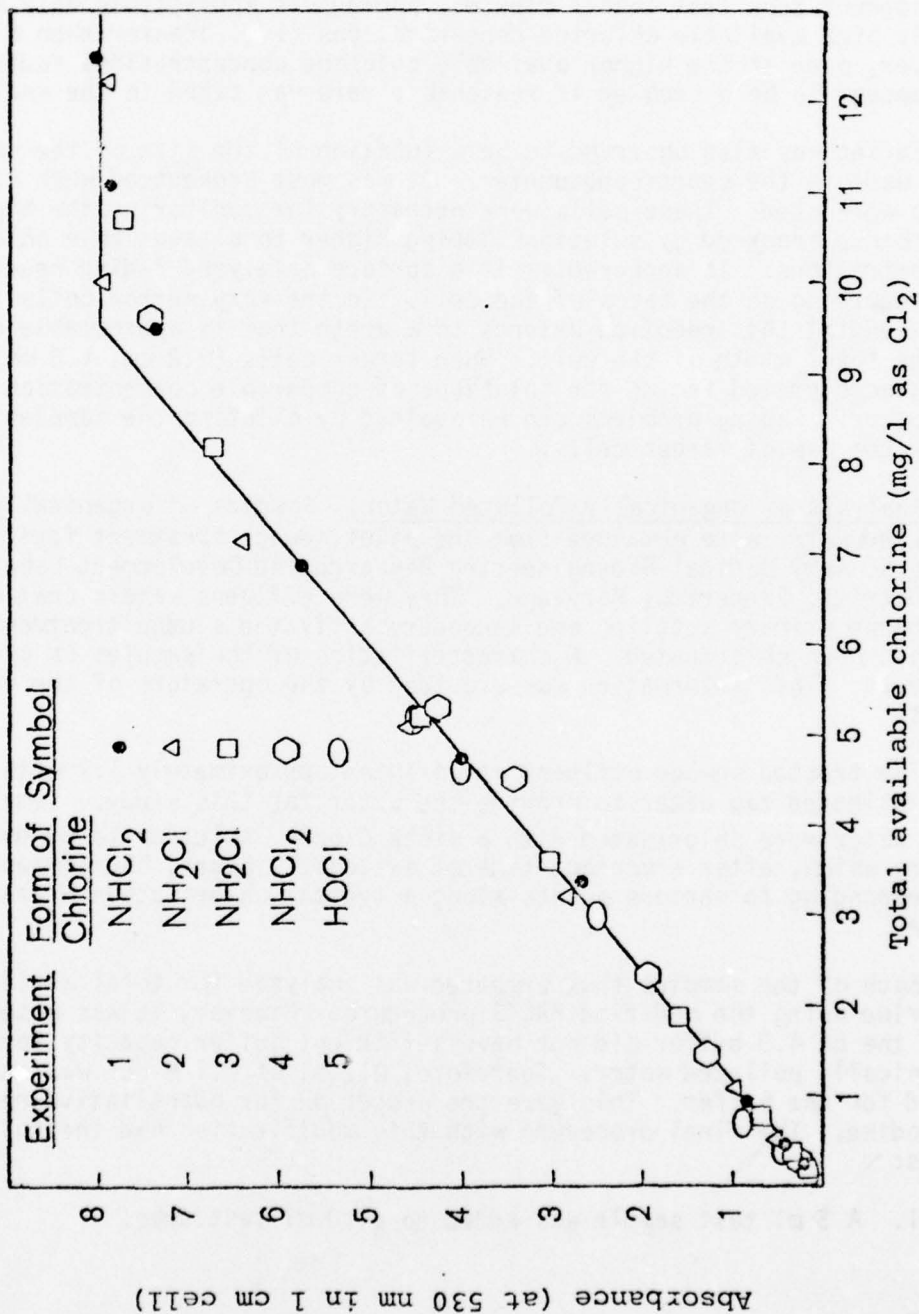
Fig.8. Beer's Law Plot for the modified FACTS procedure

Experiment	Form of Chlorine	Symbol
1	$NHCl_2$	●
2	NH_2Cl	△
3	NH_2Cl	□
4	$NHCl_2$	⬡
5	$HOCl$	⬡

Absorbance (at 530 nm in 1 cm cell)

Total available chlorine (mg/1 as Cl_2)

27

Color Development and Fading for Synthetic Samples. Color develop-
ment and fading were also studied as a function of TAC concentration and
time. A plot of the data for the synthetic waters is shown in Figure 9
and the results are summarized in Table III. In all cases maximum color
development took less than 1 minute. Fading was appreciable only at rela-
tively high available chlorine concentrations (i.e. greater than 6 mg/1).
However, even at the higher available chlorine concentrations fading did
not appear to be a problem if reasonable care was taken in the analysis.

Fading was also observed to be a function of the size of the sample
cell used in the spectrophotometer. It was most pronounced when 0.1 cm
cells were used. These cells were necessary for monitoring the high
absorbance produced by solutions having higher total available chlorine
concentrations. It appeared as if a surface catalyzed fading reaction
was occurring on the faces of the cell. In the very narrow cells (0.1 cm
path length) this reaction extends to a depth that is appreciable compared
to the total width of the cell. When larger cells (0.2 cm, 1.0 cm) were
used; accelerated fading for solutions of comparable concentration did
not occur. Fading problems can be avoided by diluting the samples to
allow the use of larger cells.

Analysis of Organically Polluted Water. Samples of organically
polluted water were obtained from the pilot sewage treatment facility of
the U.S. Army Medical Bioengineering Research and Development Laboratory,
Ft. Detrick, Frederick, Maryland. They were effluent waters that had
undergone primary settling and secondary activated sludge treatment, but
had not been chlorinated. A characterization of the samples is given in
Table IV. This information was provided by the operators of the treatment
plant.

The treated sewage effluent was diluted approximately 1:2 with
dechlorinated tap water to provide the water for this study. Samples of
this water were chlorinated with a stock Clorox[R] solution to produce
waters which, after a contact time of at least 2 hours, had compositions
corresponding to various points along a typical chlorination breakpoint
curve.

Each of the samples thus prepared was analyzed for total available
chlorine using the modified FACTS procedure. However, it was observed
that the pH 4.3 buffer did not have sufficient buffer capacity for the
organically polluted water. Therefore, 0.2 ml of 0.1 M HCl was substi-
tuted for the buffer. This gave the proper pH for quantitative release
of iodine. The final procedure with this modification had the following
steps:

1. A 5 ml test sample was added to a 10 ml test tube.
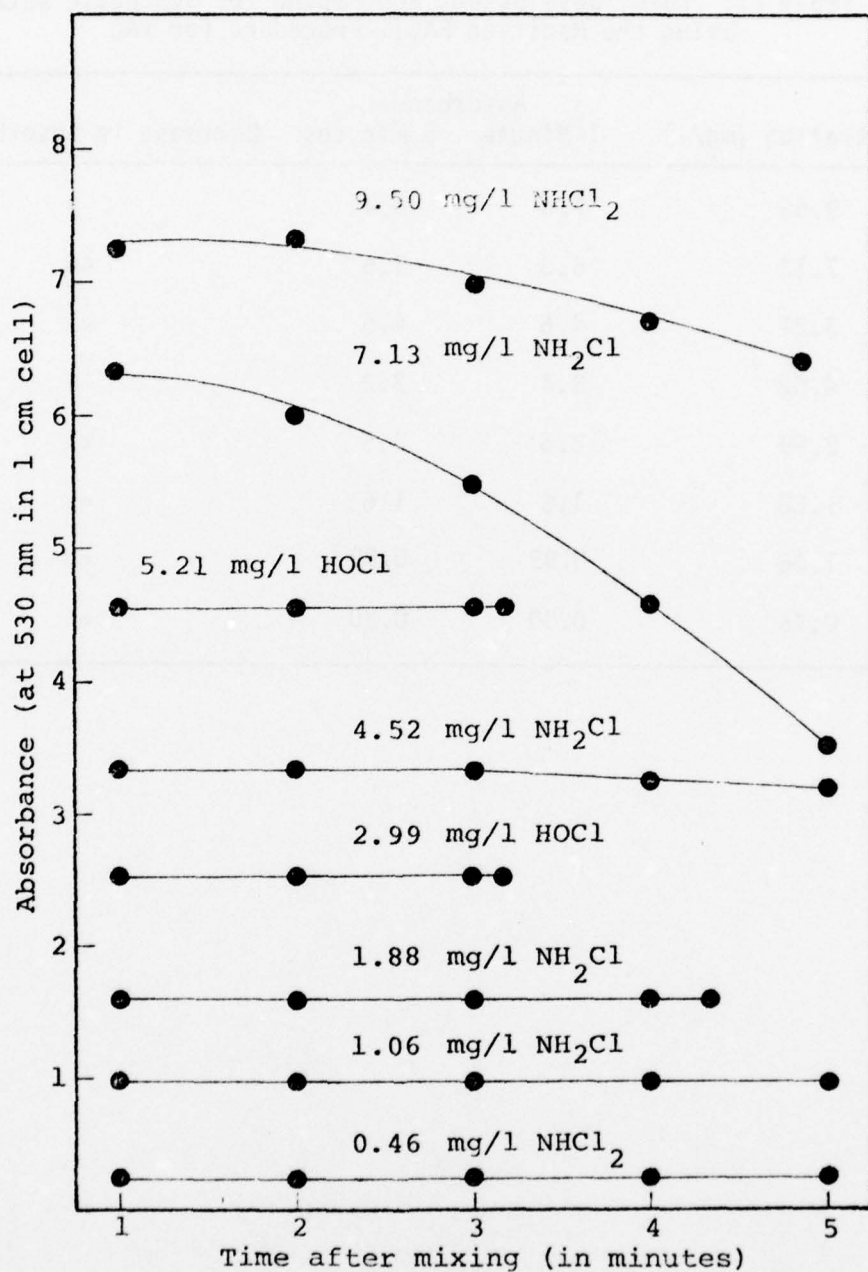
Fig. 9. Color development and fading for the modified FACTS procedure using synthetic waters. Concentrations are mg/l as Cl_2.

29

Table III Color Development and Fading for Synthetic Water
Using the Modified FACTS Procedure for TAC

Concentration (mg/l)	Absorbance		Decrease in Absorbance (%)
	1 Minute	5 Minutes	
9.50	7.3	6.4	8
7.13	6.3	3.5	44
3.21	4.6	4.6	<1
4.52	3.4	3.2	6
2.99	2.5	2.5	<1
1.88	1.6	1.6	<1
1.06	0.99	0.99	<1
0.46	0.30	0.30	<1

Table IV Characterization of Organically Polluted Water

Characteristic (mg/l)	Sample Obtained 8-10-77	Sample Obtained 8-16-77
pH	6.9	7.0
Conductivity (µmhos)	380	420
Total carbon	53	50
Inorganic carbon	37	34
Organic carbon	16	16
Ammonia-nitrogen	10	7
Nitrite-nitrogen	0.04	Not available
Nitrate-nitrogen	0.04	Not available
Iron	<0.1	<0.1
Magnesium	20	29
Calcium	143	215

2. Two tenths ml of dilute HCl (0.1 M) was added and the tube was capped and inverted to mix.

3. Four tenths ml of KI solution (12.34 g/l) was added and the tube was capped and inverted to mix.

4. Five tenths ml of pH 6.6 buffer (0.5 M phosphate) was added and the tube was capped and inverted to mix.

5. Two ml of syringaldazine indicator (118 mg/l in 2-propanol) was added and the tube was capped and inverted to mix.

6. The absorbance of the solution at 530 nm was determined with a spectrophotometer after 1 minute of reaction time.

Absorbance readings were substituted into the equation for the calibration curve and total available chlorine concentrations were calculated.

In order to check the accuracy of this procedure, each test sample was also analyzed for total available chlorine by amperometric titration. A comparison of the results given by the two methods is tabulated in Table V.

The results of the comparison to the amperometric titrator are also shown graphically in Figure 10. Assuming a 45° line through the origin, the variance was calculated by the equation below:

$$V = \frac{\sum_{i=1}^{n} d_i^2}{n}$$

where n = number of determinations

d = difference between the amperometric value and the modified FACTS result

The variance was 0.413 yielding a standard deviation (the square root of the variance) of 0.643. In every case error was less than 20 percent which would be acceptable in a field test kit for the range 0 to 10 mg/l (as Cl_2).[6,7]

Samples 8, 9, 11 and 12 were tested after they had been diluted. The results for these four samples indicate that the range of this procedure could be extended by dilution if necessary.

32

Table V Amperometric Titrator vs Modified FACTS for TAC in
Organically Polluted Waters

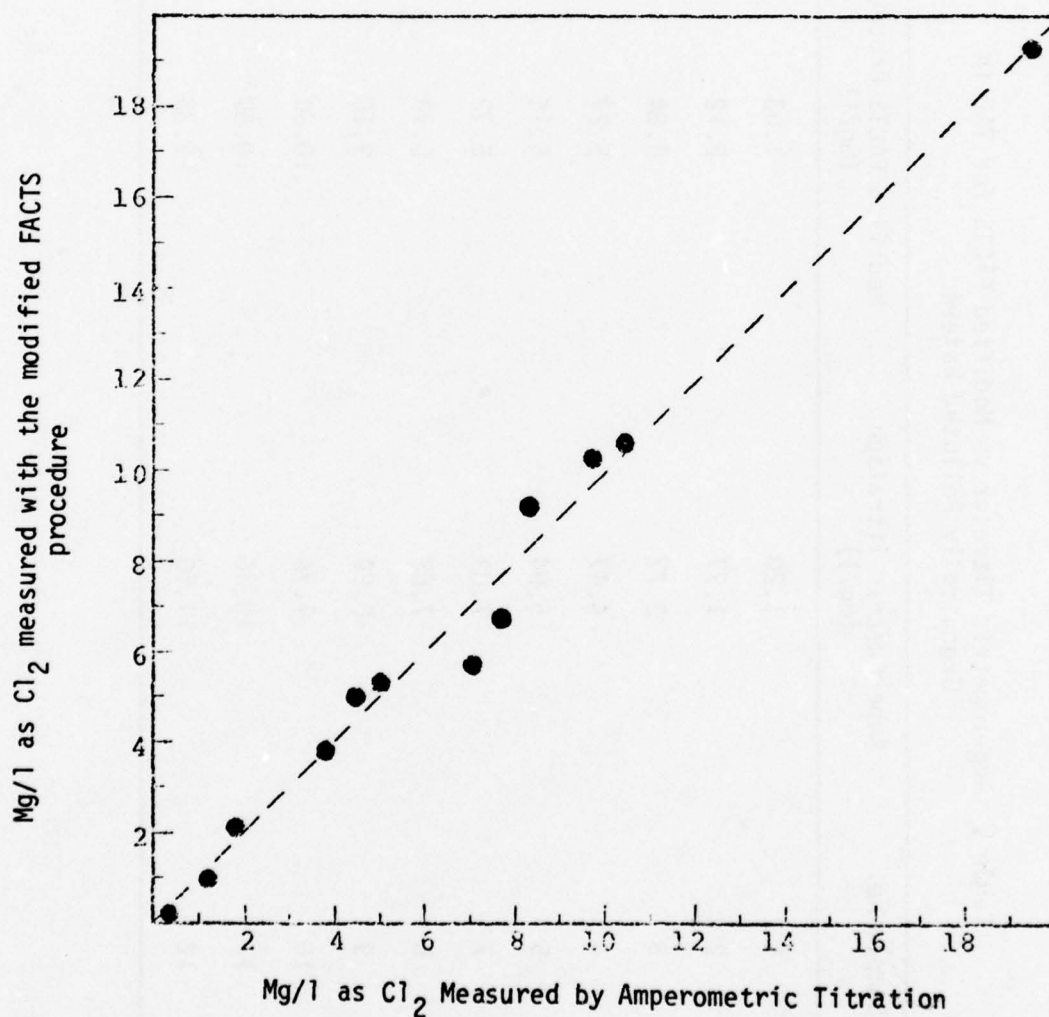| Sample No.	Amperometric Titration (mg/1)	Modified FACTS Procedure (mg/1)
1	1.20	1.03
2	1.77	2.12
3	3.77	3.84
4	4.47	5.27
5	5.04	5.16
7	7.09	5.72
8	7.67	6.70
9	8.29	9.16
10	9.74	10.30
11	10.36	10.59
12	19.50	19.33

Fig. 10. Comparison of total available chlorine concentration measured with the modified FACTS procedure and the total available chlorine concentration measured with the Amperometric Titrator.

34

Color Development and Fading in Organically Polluted Samples. Color
development and fading are shown in Figure 11 and Table VI for the organi-
cally polluted samples. The curves shown in this figure were for selected
cases where fading was most severe. Fading is not a problem during the
time span needed to make an analysis. A comparison to Figure 9 where
fading for synthetic water was shown, indicates that fading may be more
likely for lower total available chlorine concentrations when the waters
are organically polluted. However, more data are needed to draw defini-
tive conclusions.

The Effect of KI on the FACTS Procedure. Solutions of varying FAC
concentration were tested with the modified FACTS procedure with and with-
out the addition of KI. In the tests without KI addition, demand-free
water was substituted for the pH 4.3 buffer and KI solutions (steps 2 and
3). A comparison of the results obtained with the two procedures is shown
in Table VII.

The results are also shown graphically in Figure 12. The data indi-
cate that the addition of KI results in increased color production, espe-
cially at low FAC concentrations. The addition of potassium iodide in
the modified procedure was the only significant difference in the two
procedures and must, in some way, account for the additional color pro-
duced. A possible explanation would be the presence of an active com-
pound in the test solutions or reagents that liberated additional iodine
in the test procedure or reacted with FAC to lower the observed FAC con-
centration. Such a compound could be an impurity in any of the solutions
or a contaminant from the glassware used. Chlorine demand due to solvent
or dirty glassware would result in combined available chlorine which
would not react directly with syringaldazine, but which would react with
iodide in the modified FACTS procedure. This reaction with a combined
available chlorine species in addition to the reaction with FAC would
account for the greater absorbance given by the modified procedure.

Since all glassware used was made demand-free and all water used for
solutions and dilutions was demand-free, any chlorine demand must result
from syringaldazine indicator solution. This assumption agrees with the
observation that some indicator solutions gave consistantly lower results
than were observed in the initial FACTS study.[12] Indicator solutions
differing only in the source of the 2-propanol used as indicator solvent
gave results which varied greatly for the same concentration of FAC.
These observations would tend to indicate that there is some impurity in
the 2-propanol that creates a chlorine demand. Further study is required
to solve this problem.

The results presented in Table VII were obtained with a good indi-
cator solution that gave a color response identical to that achieved in
the earlier studies.[12]

35
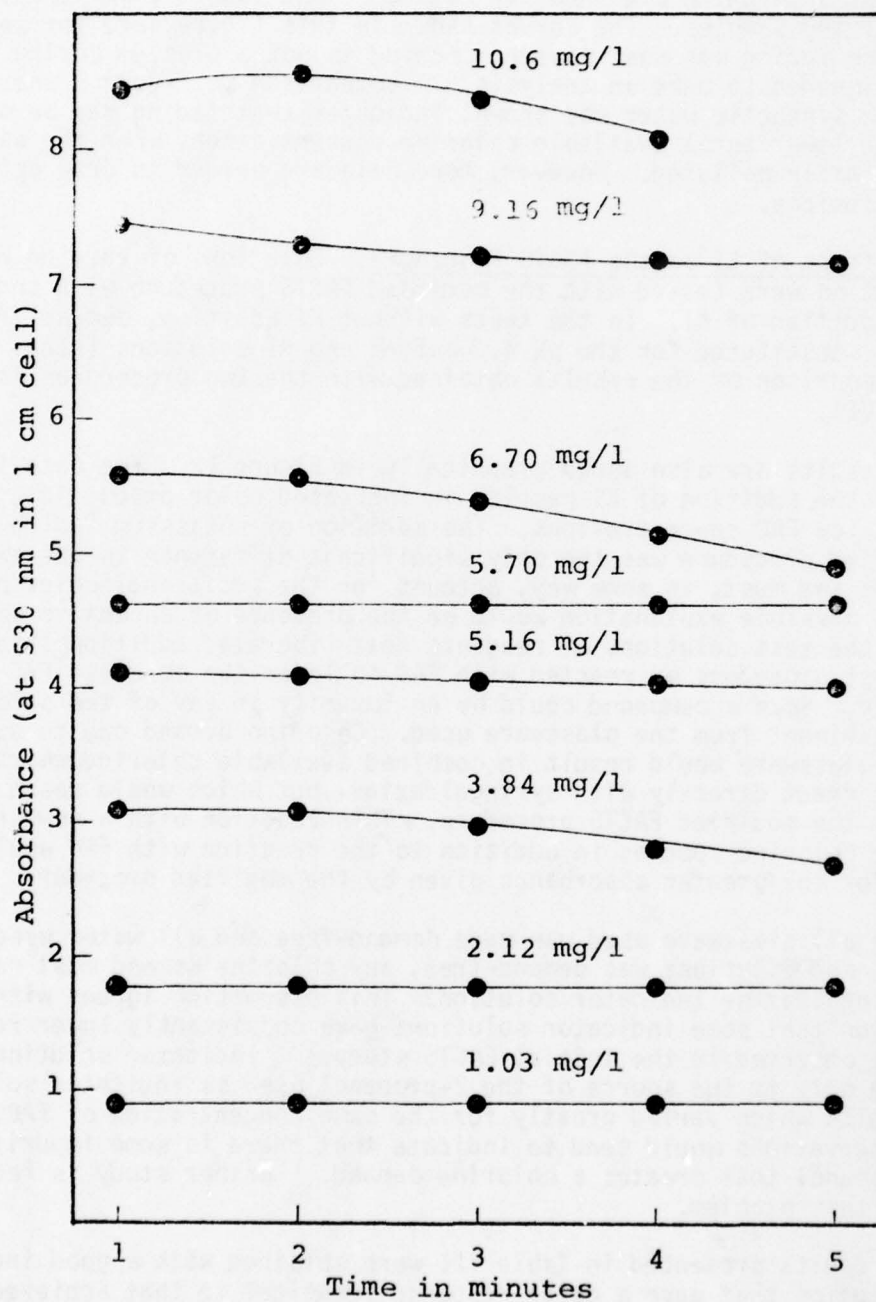
Fig.11. Color development and fading for the modified FACTS procedure using organically polluted water.

Table VI Modified FACTS Procedure for TAC Color Development
and Fading - Organically Polluted Water

Concentration (mg/l as Cl$_2$)	Absorbance		Decrease in Absorbance (%)
	1 Minute	5 Minutes	
10.6	8.5	8.1	5
9.16	7.5	7.2	4
6.70	5.6	4.9	12
5.72	4.6	4.6	<1
5.16	4.2	4.0	5
3.84	3.1	2.7	13
2.12	1.8	1.8	<1
1.03	0.90	0.90	<1

Table VII   Comparisons of Results of FACTS with and without KI

mg/l as Cl_2	Absorbance Modified FACTS	Absorbance Modified FACTS w/o KI
0.226	0.136	0.012
0.284	0.227	0.084
0.470	0.407	0.208
0.979	0.878	0.586
1.56	1.412	0.987
2.99	2.54	2.02
5.21	4.56	3.64

38
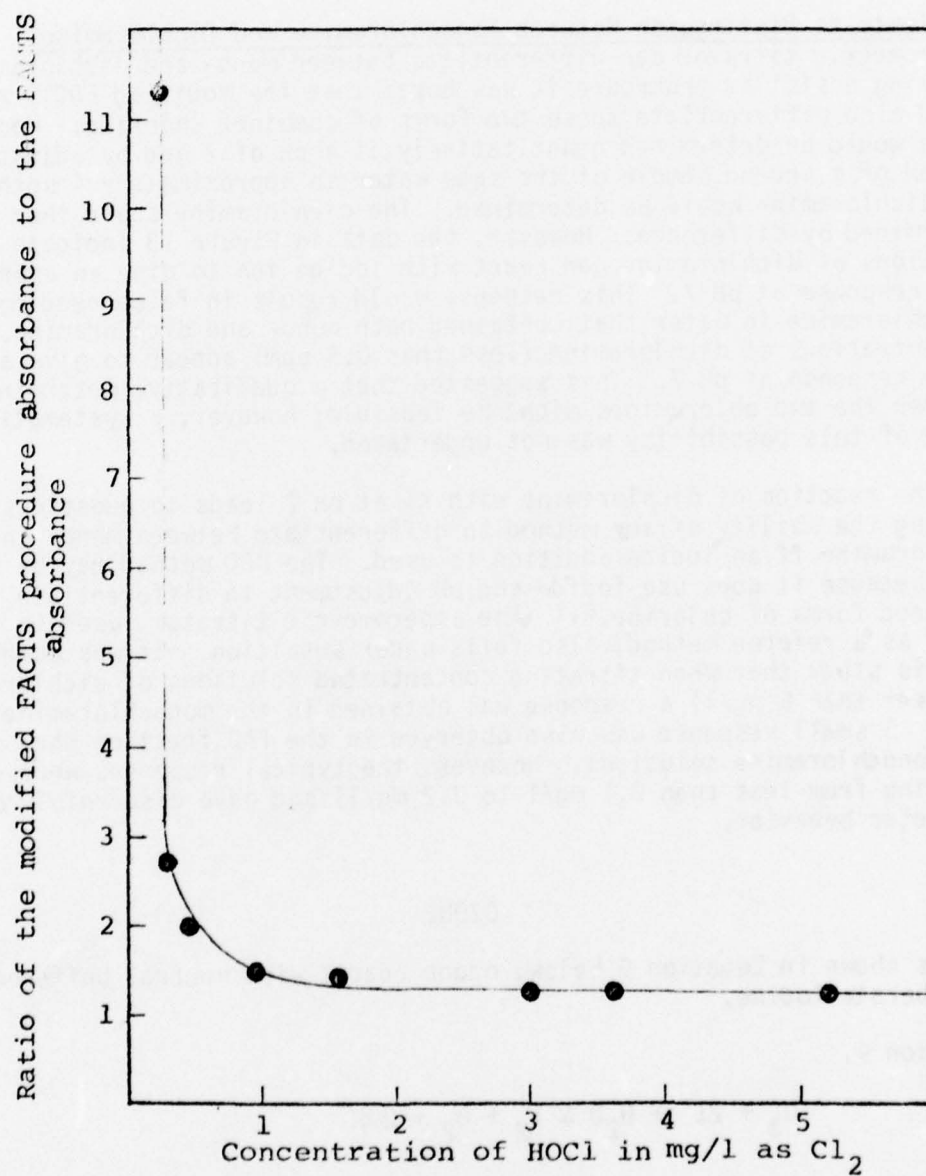
Fig. 12. Comparison of the modified FACTS
procedure absorbance to the FACTS absorbance.

The data presented in Figure 12 demonstrate that differences due to addition of iodide ion were more significant at low concentrations of FAC. The ratio of the absorbance produced by the modified FACTS procedure to the absorbance produced by the FACTS procedure decreased and became almost constant as the concentration of FAC increased. This is indicative of a constant chlorine demand which would have a larger relative effect at the lower concentrations of FAC.

Tests to Distinguish Between Monochloramine and Dichloramine. The amperometric titrator can differentiate between mono- and dichloramine. By using a similar procedure it was hoped that the modified FACTS method could also differentiate these two forms of combined chlorine. Monochloramine would be determined quantitatively at a pH of 7 and by adjusting the pH of a second sample of the same water to approximately 4 both mono- and dichloramine would be determined. The dichloramine could then be determined by difference. However, the data in Figure 13 indicate that solutions of dichloramine can react with iodide ion to give an appreciable response at pH 7. This response would result in false readings for monochloramine in water that contained both mono- and dichloramine. Low concentrations of dichloramine (less than 0.5 ppm) appear to give a negligible response at pH 7. This suggested that a qualitative determination between the two chloramines might be feasible; however, a systematic study of this possibility was not undertaken.

The reaction of dichloramine with KI at pH 7 leads to questions concerning the ability of any method to differentiate between mono- and dichloramine if an iodide addition is used. The DPD method may be suspect because it does use iodide and pH adjustment to differentiate the combined forms of chlorine.[6,7] The amperometric titrator, used in this study as a referee method, also falls under suspicion. It was observed in this study that when titrating concentrated solutions of dichloramine (greater than 5 mg/l) a response was obtained in the monochloramine fraction. A small response was also observed in the FAC fraction when titrating monochloramine solutions. However, the typical responses were small (ranging from less than 0.1 mg/l to 0.2 mg/l) and gave discernibly different meter behavior.

OZONE

As shown in Equation 9 below, ozone reacts with neutral buffered KI to liberate iodine.

Equation 9.

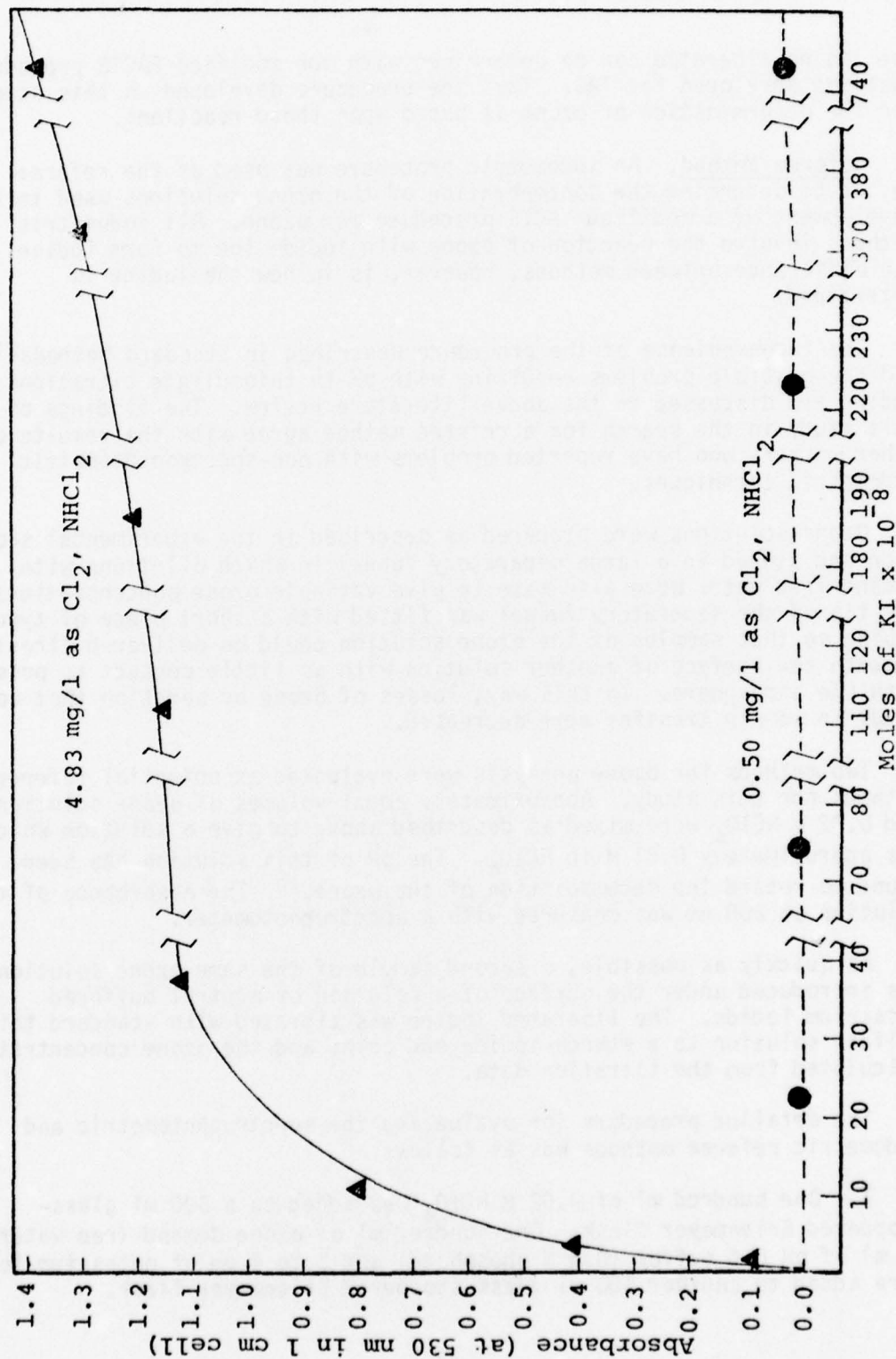$$O_3 + 2I^- + H_2O \rightleftharpoons I_2 + O_2 + 2OH^-$$
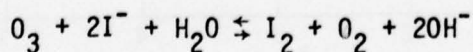
Fig. 13. Response of dichloramine to the modified FACTS procedure at pH 7. (Breakthrough).

The iodine liberated can be determined with the modified FACTS procedure that was developed for TAC. Thus the procedure developed in this study for the determination of ozone is based upon these reactions.

Referee Method. An iodometric procedure was used as the referee method to determine the concentration of the ozone solutions used in the development of a modified FACTS procedure for ozone. All iodometric methods involve the reaction of ozone with iodide ion to form iodine. The difference between methods, however, is in how the iodine is determined.

The inconvenience of the procedure described in Standard Methods[21] and the possible problems resulting with pH in thiosulfate titrations of iodine are discussed in the above literature review. The findings of this study in the search for a referee method agree with the results of other workers who have reported problems with non-spectrophotometric iodometric techniques.

Ozone solutions were prepared as described in the experimental section and stored in a large separatory funnel in which dilutions with demand-free water were also made to give variable ozone concentrations. The tip of the separatory funnel was fitted with a short piece of tygon tubing so that samples of the ozone solution could be delivered directly beneath the surface of another solution with as little contact as possible with the atmosphere. In this way, losses of ozone by aeration that could occur in sample transfer were decreased.

Two methods for ozone analysis were evaluated as potential referee methods for this study. Approximately equal volumes of ozone solution and 0.02 M $HClO_4$ were mixed as described above to give a solution which was approximately 0.01 M in $HClO_4$. The pH of this solution has been found to retard the decomposition of the ozone.[30] The absorbance of this solution at 260 nm was measured with a spectrophotometer.

As quickly as possible, a second sample of the same ozone solution was introduced under the surface of a solution of neutral buffered potassium iodide. The liberated iodine was titrated with standard thiosulfate solution to a starch-iodide end point and the ozone concentration calculated from the titration data.

The detailed procedure for evaluating the spectrophotometric and iodometric referee methods was as follows:

1. One hundred ml of 0.02 M $HClO_4$ was added to a 500 ml glass-stoppered Erlenmeyer flask. One hundred ml of ozone demand-free water, 16 ml of pH 6.6 buffer (0.5 M phosphate) and 3 to 4 gm of potassium iodide were added to another 500 ml glass-stoppered Erlenmeyer flask.

2. Both flasks were weighed to the nearest hundreth of a gram.

3. Approximately 200 ml of ozone solution to be analyzed was delivered beneath the surface of the solutions in each of the flasks. This was done as quickly as possible to assure that both flasks received identical ozone concentrations.

4. Both flasks were weighed to the nearest hundreth of a gram to determine the weight of ozone sample added.

5. As quickly as possible, a sample from the flask containing ozone in perchloric acid was placed in a 5 cm quartz cell and the absorbance measured at 260 nm with a spectrophotometer. Steps 3, 4, and 5 were performed as quickly as possible to assure minimal loss of ozone during the analysis.

6. Three 100 ml aliquots from the flask containing iodide were titrated with a standard thiosulfate solution to the starch-iodide end point.

Assuming that the densities of the solutions in both flasks were essentially the same as that of water (1 g/ml), the final volumes in each flask were determined from the weight of the ozone sample (the difference in weight between steps 2 and 4). The absorbance readings from step 5 were corrected for cell path length and dilution. Ozone concentrations from step 6 were calculated using the iodine concentration determined by thiosulfate titration and corrected for dilution. A one-to-one molar ratio of ozone to iodine was assumed since the iodine was liberated at neutral pH. The ozone concentration determined iodometrically was used to calculate the molar extinction coefficient from the absorbance at 260 nm. Values of the molar extinction coefficient calculated from data collected on four consecutive days are shown in Table VIII. The Beer's Law curves used to calculate these values are shown in Figure 14. The results were not reproducible on a day to day basis and were below the value of 2.9×10^3 l mole^{-1} cm^{-1} cited in the literature.[30,31] These low values obtained can be accounted for by a molar ratio of iodine to ozone of greater than 1:1. Extra iodine may have been generated when the pH was dropped for the thiosulfate titration.

No explanation was found for the lack of daily reproducibility in the values obtained. Since modifications to the above volumetric method gave no improvement in accuracy or reproducibility, another spectrophotometric procedure was used as the referee method. This spectrophotometric method is based upon the absorbance of the triiodide ion at 352 nm.[25] It is believed to be more accurate because the pH is kept at 7 during and after the liberation of iodine. The experimental procedure involved the following sequence of steps:

Table VIII   Molar Extinction Coefficient of
Ozone at 260 nm Determined Iodometrically

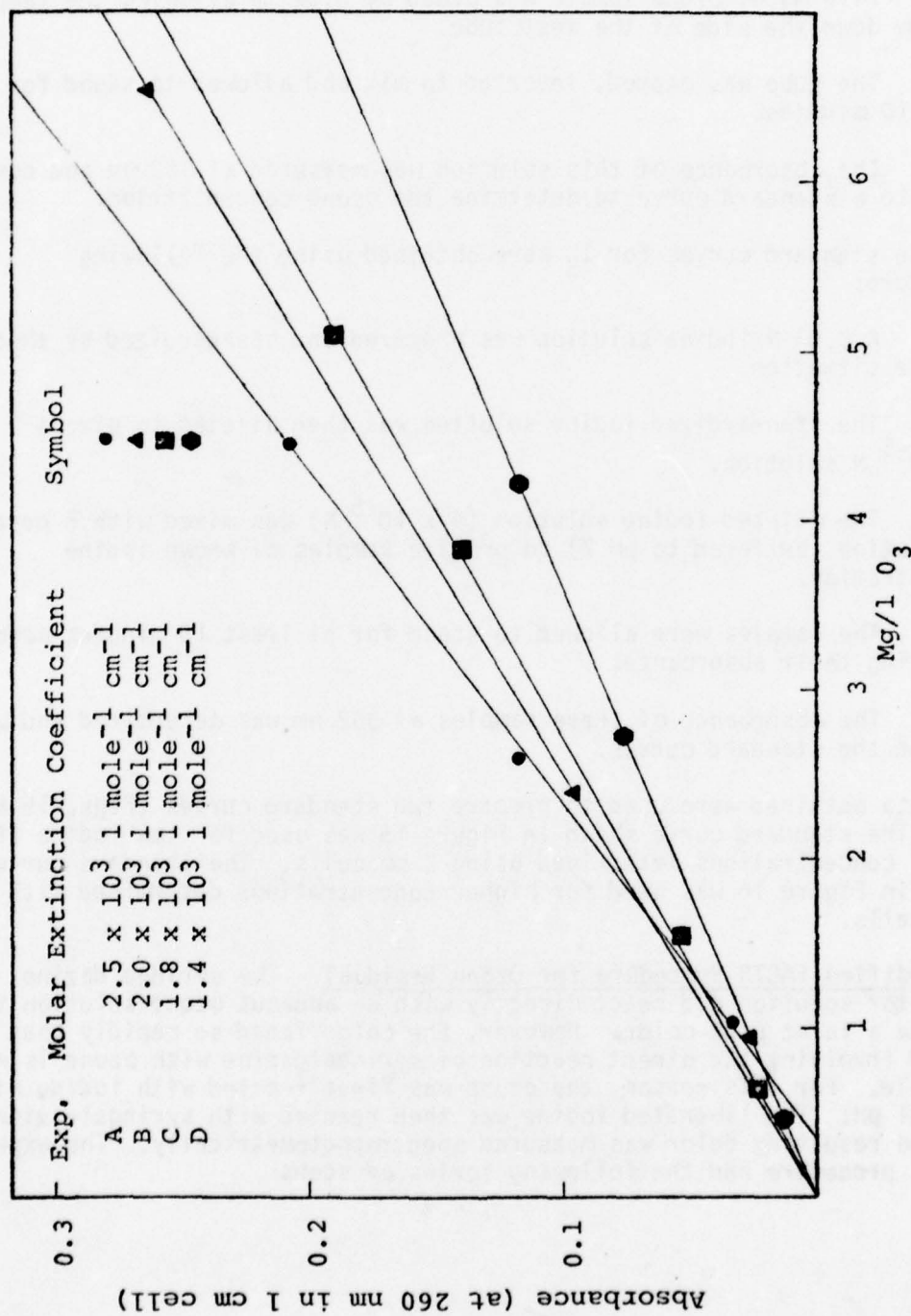| Experiment	Molar Extinction Coefficient ($1 \text{ mole}^{-1} \text{ cm}^{-1}$)
A	2.5×10^3
B	2.0×10^3
C	1.8×10^3
D	1.4×10^3

44

Fig.14. Plots used to determine the molar extinction coefficient of ozone.

1. Five ml of 5 percent KI solution (buffered to pH 7) was added to a 12 ml test tube.

2. Five ml of ozone sample was added by pipette allowing the sample to flow down the side of the test tube.

3. The tube was capped, inverted to mix and allowed to stand for at least 10 minutes.

4. The absorbance of this solution was measured at 352 nm and compared to a standard curve to determine the ozone concentration.

The standard curves for I_3 were obtained using the following procedure:

1. A 0.01 N iodine solution was prepared and standardized by thiosulfate titration.

2. The standardized iodine solution was then diluted to give a 4×10^{-5} N solution.

3. The diluted iodine solution (4×10^{-5} N) was mixed with 5 percent KI solution (buffered to pH 7) to provide samples of known iodine concentration.

4. The samples were allowed to stand for at least 10 minutes before measuring their absorbance.

5. The absorbance of these samples at 352 nm was determined and used to plot the standard curves.

The data obtained were used to prepare two standard curves (Figs. 15 and 16). The standard curve shown in Figure 15 was used for low iodine (i.e. ozone) concentrations determined using 2 cm cells. The standard curve shown in Figure 16 was used for higher concentrations determined with 1 cm cells.

Modified FACTS Procedure for Ozone Residual. The syringaldazine indicator solution did react directly with an aqueous ozone solution to produce a faint pink color. However, the color faded so rapidly that a method involving the direct reaction of syringaldazine with ozone is not possible. For this reason, the ozone was first reacted with iodide at a neutral pH. The liberated iodine was then reacted with syringaldazine and the resulting color was measured spectrophotometrically. The experimental procedure had the following series of steps:
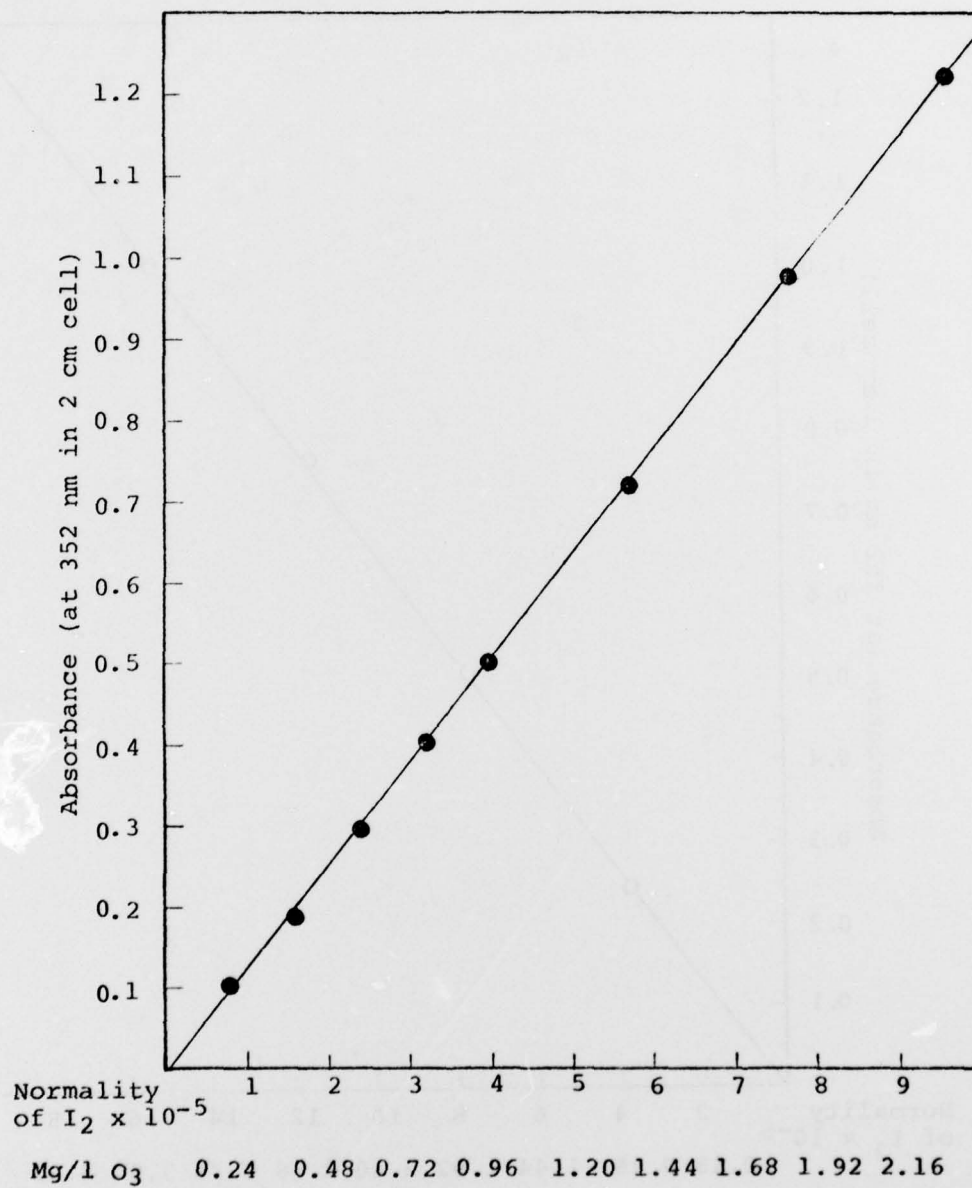
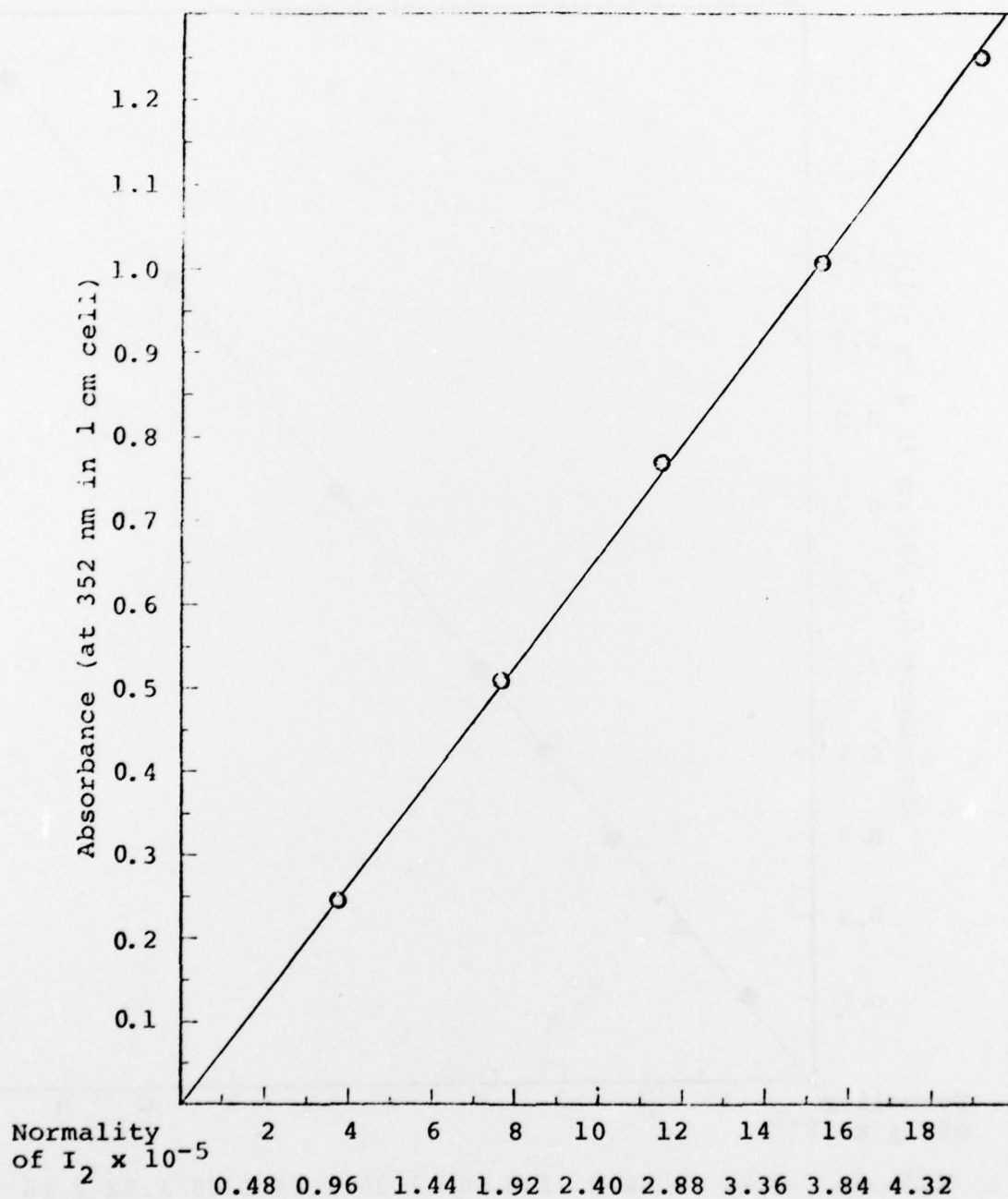Fig.15. Standard iodine curve in the range of
0.24 mg/l O_3 to 2.16 mg/l O_3.

Fig.16. Standard iodine curve in the range of 0.48 mg/l O_3 to 4.80 mg/l O_3.

48

1. Five ml of 5 percent KI (buffered at pH 7) was added to a 12 ml test tube (tube 1).

2. Five ml of ozone sample was added and the tube was capped and inverted to mix. The tube was set aside for at least 10 minutes.

3. Five tenths ml of pH 6.6 buffer (0.5 M phosphate) was added to a 10 ml test tube (tube 2).

4. Five tenths ml of KI solution (12.34 g/l) was added to tube 2. The tube was capped and inverted to mix.

5. Five ml of ozone sample from step 2 was added to tube 2. The tube was capped and inverted to mix.

6. Two ml of syringaldazine indicator solution (118 mg/l in 2-propanol) was added to tube 2. The tube was capped and inverted to mix.

7. The absorbance of the solution (tube 2) at 530 nm was measured with a spectrophotometer. Color development and fading were monitored as a function of time. The absorbance at 352 nm of the solution from step no. 1 was also measured with the spectrophotometer to determine the concentration of the ozone solution being tested.

The results obtained with the modified FACTS procedure are shown in Figure 17. As can be seen, agreement with Beer's Law was excellent and allowed determination of ozone concentrations as high as 6 mg/l as O_3. Higher ozone concentrations can be determined by dilution of samples, but ozone concentrations greater than this are rarely encountered in water treatment.

All of the data collected were analyzed by least squares linear regression to obtain the following equation which best represents the linear portion of the curve:

$$A = 1.49 [O_3] - 0.0619$$

where A = the absorbance

$[O_3]$ = concentration of ozone in mg/l O_3.

Figure 18 shows the color development and fading for the ozone solutions tested as a function of concentration. The fading data are also summarized in Table IX. The color development reached a maximum within the time needed for the analysis and fading was not severe for the samples tested.
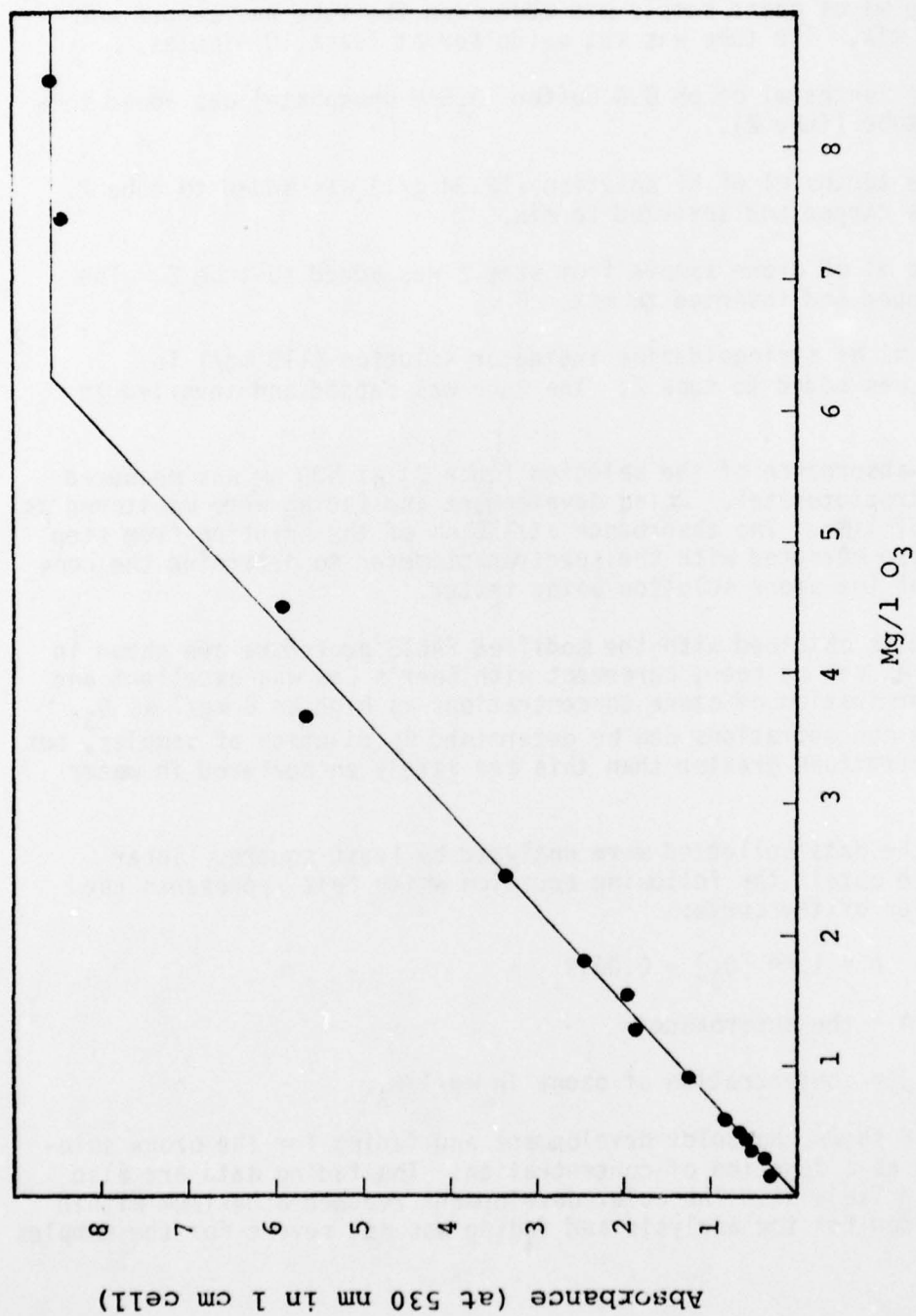
Fig.17. Beer's Law plot for the determination of ozone using
the modified FACTS procedure.

50
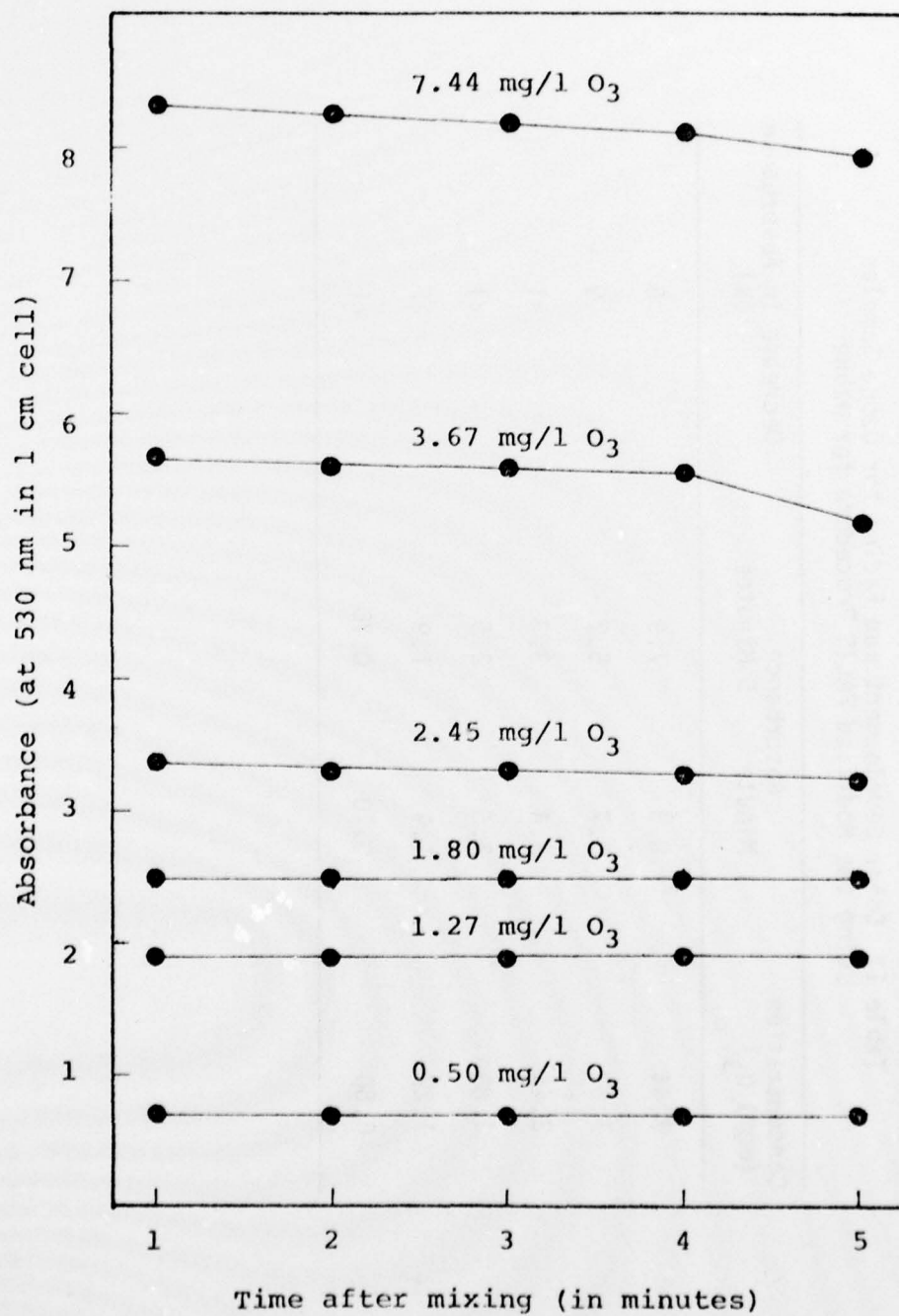
Fig.18. Color development and fading for ozone determination with the modified FACTS procedure.

51

Table IX Color Development and Fading For Ozone Samples
Using the Modified FACTS Procedure for Ozone

Concentration (mg/l O_3)	Absorbance 1 Minute	Absorbance 5 Minutes	Decrease in Absorbance (%)
7.44	8.3	7.9	5
3.67	5.7	5.2	9
2.45	3.4	3.3	<1
1.80	2.5	2.5	<1
1.27	1.9	1.9	<1
0.50	0.70	0.70	<1

52

CONCLUSIONS

Chlorine

The FACTS procedure has been modified to determine total available chlorine in aqueous solutions. This method was shown to be simple, accurate, and precise for analysis of standardized samples of total available chlorine (TAC). It has been used to analyze organically polluted water and was found to give acceptable results as determined by comparison to amperometric titration of the same samples. However, the buffer in the procedure had to be modified to buffer the high alkalinity.

The modified FACTS procedure for TAC obeys Beer's Law through the range of 0-10 mg/1 TAC (as Cl_2). The lower limit of sensitivity was shown to be approximately 0.2 mg/1 (as Cl_2).

The maximum color was found to develop within 1 minute and for most samples was stable over a period of 5 minutes. In some cases, higher concentrations of TAC did show extreme fading near the end of 5 minutes. However, fading does not appear to be a problem if reasonable care is taken in a TAC determination.

It is recommended that the 2-propanol used in the preparation of the syringaldazine indicator solution should be purified in order to remove any chlorine demand.

Although not attempted, it appears that this procedure could readily be adapted to a field test kit for determining free available chlorine and total available chlorine in water.

Ozone

The FACTS procedure has also been modified to determine residual ozone in aqueous solutions. This method was shown to be simple, accurate, and precise for determining ozone concentrations in laboratory produced waters. It obeys Beer's Law through the range 0-6 mg/1 O_3 and has a lower limit of sensitivity of approximately 0.2 mg/1 O_3.

As with the procedure for TAC, color development was complete within a minute and fading over most of the applicable concentration range does not appear to be a problem as long as reasonable care is exercised in the analysis.

It is recommended that the FACTS procedure for ozone undergo further evaluation at a water treatment plant employing ozonation. This would allow evaluation of the procedure under actual conditions on organically polluted waters.

53

EXPERIMENTAL

General

Spectrophotometer. All spectrophotometric measurements were made on a Beckman ACTA (CV) spectrophotometer. Measurements were made at room temperature. The spectrophotometer was equipped with time drive and repetitive scan functions to facilitate observations with time.

Glassware. All glassware was cleaned with potassium dichromate/sulfuric acid solution followed by dilute HCl and distilled water rinses.

Potassium Iodide Solutions. The 12.34 g/l potassium iodide (Reagent ACS KI, Fisher Scientific) solutions were prepared in chlorine demand-free water and in ozone demand-free water. These stock iodide solutions were diluted as necessary with the appropriate demand-free water.

Buffer Solutions. Stock buffer solutions 0.5 M in potassium phosphate, KH_2PO_4 (Analytical Reagent, Mallinckrodt), and 0.5 M in sodium dibasic phosphate monohydrate, $Na_2HPO_4 \cdot H_2O$ (Certified grade, Fisher Scientific) were prepared in chlorine demand-free water and in ozone demand-free water. *The pH of each buffer was approximately 6.6.*

Syringaldazine Indicator Solution. Syringaldazine (Aldrich Chemical Co.), 118 mg, was dissolved in reagent grade 2-propanol (Matheson, Coleman and Bell, Reagent ACS) and diluted to 1 liter. Solution of syringaldazine was aided by the use of an ultrasonic bath. These solutions were tested to verify that the response obtained was identical to the response observed during the initial development of the FACTS procedure. This was done by comparing the absorbance obtained with a known FAC concentration to the value calculated from the equations reported in the earlier study.[12] An indicator was judged acceptable if it produced a color within 5 percent of the calculated value.

Chlorine

Chlorine Demand-Free Glassware. After being cleaned as previously described, all glassware was soaked in water with a FAC level of at least 10 mg/l. This glassware was rinsed with chlorine demand-free water immediately before use.

Chlorine Demand-Free Water. All waters used for the chlorine studies were made chlorine demand-free. This was achieved by adding Clorox[R] to distilled water to produce an FAC residual of at least 1 mg/l after 12 hours contact time, and then removing the FAC residual by dechlorination in sunlight. The water was periodically tested for FAC with the

FACTS II procedure.[12] Potassium iodide was added prior to the Facts II analysis to determine if combined available chlorine was present. Chlorine demand-free water prepared by the above procedure was dispensed through a siphon system. Air used to displace the siphoned water was first passed through a 50 percent H_2SO_4 trap to avoid ammonia and amine contamination.

Referee Method. Amperometric titration was used to standardize all solutions containing chlorine as free available chlorine or combined chlorine. The procedure used is found in Standard Methods[21] and has been presented elsewhere.[32,33] A Fischer & Porter Amperometric titrator (Model 17T1010) was used throughout the study.

Stock Chlorine Solutions. Stock solutions of free available chlorine (FAC), 500 mg/l as Cl_2, were prepared by diluting 10 ml of Clorox[R] to 1 liter with demand-free water. This stock solution was standardized by the iodometric method.[21]

Monochloramine and Dichloramine Solutions. Both chloramine solutions were prepared by the method of Johnson.[34] In preparing the solutions a minimum of a three to one molar ratio of ammonium chloride to chlorine was necessary. The ammonium chloride (Reagent ACS, granular, B and A Allied Chemicals) was used as received.

Equal volumes of stock chlorine solution (500 mg/l as Cl_2) and ammonium chloride solution (12.336 g/l) were mixed with stirring to produce a stock monochloramine solution of approximately 250 mg/l (as Cl_2). The chlorine solution was added to the ammonium chloride solution to assure that ammonia was always in excess during preparation of monochloramine. This stock monochloramine solution was then diluted with demand-free water to give varying monochloramine concentrations. Solutions were standardized each day by amperometric titration.

Dichloramine solutions were prepared in the same manner; but, the pH of the solution was lowered to approximately 4 by addition of dilute hydrochloric acid after mixing the ammonium chloride with FAC. The solutions were allowed to stand overnight in a brown glass-stoppered bottle before standardization. The dichloramine solutions were standardized immediately before use.

Buffers. Buffers of varying pH were prepared in chlorine demand-free water by mixing varying proportions of 0.5 M KH_2PO_4 and 0.5 M $Na_2HPO_4 \cdot H_2O$. The pH of each buffer was determined by a standardized pH meter and ranged from approximately 4 to 9.

55

Buffers for pH values below 4 were made by adding dilute hydrochloric acid to 0.5 M KH_2PO_4.

Ozone

Generation of Ozone. The ozone used in this study was produced by a Grace Ozone Generator manufactured by the Grace Chemical Division. This generator uses electric discharge in oxygen or in air to produce ozone. In this study, oxygen (Linde Division, Union Carbide Corp.) without any pretreatment was passed through the generator. It was assumed that the mixture of ozone and oxygen coming from the generator outlet was a maximum of 6 percent by volume ozone.[20] Knowledge of ozone concentration in the gas stream or even day-to-day reproducibility of ozone concentration in the gas stream was not necessary for this study; however, the power control and the pressure control on the ozone generator were adjusted to the same values for each sample. These settings were 300 watts and 3 lb/in^2, respectively. At these settings, the volume of ozonated oxygen produced by the generator was one SCFH (standard cubic feet per hour).

The ozone generator was connected by tygon tubing to a gas collecting flask fitted with a sparger. The ozone-oxygen mixture was then bubbled for at least 2 minutes through the water in the gas collecting flask.

Ozone Demand-Free Glassware. All glassware used in the ozone analysis was soaked in strong ozone solutions for at least 15 minutes. After soaking, the glassware was rinsed in ozone demand-free water and then placed in an oven at approximately 100°C for at least 10 minutes to insure that the ozone had been dissipated.

Ozone Demand-Free Water. Because ozone is such a strong oxidizing agent and reacts with so many species that might be present in even the most carefully distilled water, it was necessary to prepare ozone demand-free water. First, normal laboratory distilled water was glass-distilled. This glass-distilled water was ozonated as described in the previous section. The ozonated water was then boiled for at least 15 minutes to remove any remaining ozone or ozone decomposition products. The water was cooled to room temperature before use. This water was also checked on a spectrophotometer at 260 nm to insure that all the ozone had been boiled off.

This procedure produced ozone demand-free water which was used for all solutions that would come in contact with ozone before analysis. All dilution water and rinse waters were also ozone demand-free.

Ozone Solutions. Ozone demand-free water was ozonated immediately before use as described in the section on generation of ozone. Spectrophotometric analysis demonstrated that saturated solutions of ozone were

produced. These solutions had to be diluted with ozone demand-free water to produce solutions with realistic ozone concentrations (0 to 5 ppm) and to make solutions that were reasonably stable over the short period of time needed for analysis. If the more concentrated solutions were not diluted, agitation or pouring caused immediate, and drastic changes in ozone concentration.

Thiosulfate Solution. A sodium thiosulfate solution (Anhydrous, Certified ACS, Fisher Scientific) was prepared in laboratory distilled water for the iodometric titrations. The solution was standardized several times during the study using the bi-iodate technique found in Standard Methods.[21] The bi-iodate used was a Fisher Scientific Standard solution.

Perchloric Acid Solution. A 0.02 M $HClO_4$ solution was prepared in ozone demand-free water using Baker reagent grade 70 percent perchloric acid.

Neutral-Buffered Potassium Iodide Solution. This solution was prepared as described by Schechter[25] using ozone demand-free water and contained 20.0 g of potassium iodide (Fisher laboratory grade) in disodium hydrogen phosphate. This solution was kept in a refrigerator when not in use.

Standard Iodine Solution. An iodine solution (ca. 0.01 N) was made up in distilled water and aged 1 day. This solution was standardized immediately before use by thiosulfate titration using Thyodene (Fisher Scientific starch-iodine indicator) as the indicator. Other standard iodine solutions of varying concentration were made by diluting this solution.

BIBLIOGRAPHY

1. A.T. Palin, "Chemistry and Control of Modern Chlorination," LaMotte Chemical Products Co., Chestertown, MD (1973).

2. S.L. Chang, J. San. Eng. Div. Proc. ASCE, 97, 689 (1971).

3. A.E. Griffin, J. Am. Water Works Assoc., 32, 1187 (1940).

4. G.C. White, J. Am. Water Works Assoc., 43, 201 (1951).

5. I.W. Wei, "Chemistry of Breakpoint Chlorination," presented before the Division of Environmental Chemistry, American Chemical Society, New Orleans, Louisiana, March 1977, pp 240-241.

6. C. Sorber, W.J. Cooper, and E. Meier in "Disinfection Water and Wastewater," J.D. Johnson, Ed., Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan, 1975, Chapter 5.

7. K.J. Guter, W.J. Cooper, and C.A. Sorber, J. Am. Water Works Assoc., 66(1), 38 (1974).

8. A.P. Black and G.P. Whittle, J. Am. Water Works Assoc., 59, 607 (1967).

9. A.T. Palin, J. Am. Water Works Assoc., 49, 873 (1957).

10. J.D. Johnson and R. Overby, Anal. Chem., 41, 1744 (1969).

11. R. Bauer and C. Rupe, Anal. Chem., 43, 421 (1971).

12. W.J. Cooper, C.A. Sorber, and E. Meier, J. Am. Water Works Assoc., 67(1), 34 (1975).

13. W.W. Bunn, B.B. Haas, E.R. Deane, and R.D. Kleopfer, Environ. Lett., 10, 205 (1975).

14. J.J. Rooke, Water Treatment and Examination, 23, 234 (1974).

15. J.M. Symons, T.A. Bellar, J.K. Carawell, J. Demarco, K.L. Kropp, G.G. Robeck, D.R. Seeger, C.J. Slocum, B.L. Smith, and A.A. Stevens, J. Am. Water Works Assoc., 67, 634 (1975).

16. H.F. Collins and D.G. Deaner, J. Environ. Eng. Div., 100(6), 761 (1973).

17. W.A. Brungs, J. Water Pollut. Control Fed., 45, 2180 (1973).

18. R.N. Kinman, First International Symposium on Ozone for Water and Wastewater, Washington, DC, Dec. 1973, pp 56-68.

19. J.J. McCarthy and C.H. Smith, J. Am. Water Works Assoc., 66, 718 (1974).

20. T.C. Manley and S.J. Niegowski, "Encyclopedia of Chemical Technology," Vol. 14, 2nd ed., John Wiley and Sons, Inc., New York, NY 1967, pp. 410-432.

21. "Standard Methods for the Examination of Water and Wastewater," 14th ed., American Public Health Association, New York, NY, 1975, p. 309.

22. R.N. Dietz, J. Pruzansky, and J.D. Smith, Anal. Chem., 45, 402 (1972).

23. A. Hodgeson, R.E. Baumgardner, B.E. Martin, and K.A. Re, Anal. Chem. 43, 1123 (1971).

24. S.L. Kopczynski and J.J. Bulfalini, Anal. Chem., 43, 1126 (1971).

25. H. Shechter, Water Research, 7, pp 729-739 (1973).

26. W.A. Boyd, C. Willis, and R. Cyr, Anal. Chem., 42, 670 (1970).

27. J.N. Pitts, Jr., J.M. McAfee, W.D. Long, and A.M. Winer, Environ. Sci. Tech., 10, 787 (1976).

28. M.G. Alder and G.R. Hill, J. Am. Chem. Soc., 72, 1884 (1950).

29. D.H. Byers and B. Saltzman, Adv. Chem. Ser., 21, 93 (1959).

30. M.L. Kilpatrick, C.C. Herrick, and M. Kilpatrick, J. Am. Chem. Soc., 78, 1784 (1956).

31. J. Hoigne and H. Bader, Water Research, 10, 377 (1976).

32. H.C. Marks, R.R. Joiner, and F.B. Strandskov, Water Sewage Works, 95, 175 (1948).

33. H.C. Marks, D.B. Williams, and G.W. Glasgow, J. Am. Water Works Assoc., 43, 201 (1951).

34. J.D. Johnson, "Field Test for Free Chlorine and the Kinetics of Bromine Residuals," Progress Report to USAMRDC, Contract No. DA-49-193-MD-2442, p. 7, Sep 1970.

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